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CALCULATING FORMULAS FOR FINE GRAINED MINERALS ON THE BASIS OF CHEMICAL ANALYSIS

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Abstract

Data are presented showing that every element found by chemical analysis can be placed in a theoretically possible three layer lattice even when the sample is grossly impure. Therefore the fact that a possible lattice can be calculated is not proof of the mineralogical purity of the sample. The impurities may be in the form of admixtures, intergrowths or adsorbed.

Silica is likely to be the most abundant impurity of the fine grained minerals. It may occur as crystalline or amorphous forms, or as adsorbed silicate ions. Phosphate, Al, Fe or H ions may also be adsorbed. Brucite, chlorite, pyrophyllite, hydrargillite, any of the micas and possibly talc, kaolinite and halloysite may occur as occasional layers in the crystals of montmorillonite and other fine grained clays. All of these forms and kinds of impurity must be absent from the sample if complete confidence is to be placed in the calculated distribution of the ions in the lattice and in the formula that is derived from the same.

With minerals which contain tetrahedral Al ions, SiO_2, as impurity, affects the calculated values not only by increasing the number of calculated Si ions, but also by reducing the number of ions with octahedral coordination. If the total calculated octahedral ions is found to be less than 2.0 per half lattice unit, the probability is that the sample contained SiO_2 as impurity. Admixtures or intergrowths of brucite, chlorite and several other structurally related minerals affect the calculation by increasing the total octahedral cations. Since these kinds of impurities tend to cancel the effects of SiO_2 and since adsorbed ions also affect the results, the sample must be essentially free from all these kinds of impurity. Otherwise the calculated values have very little value.

Montmorillonite and glauconite probably comprise isomorphous series and the isomorphism may involve the proxying of Al ions for Si ions in tetrahedral positions of the lattice or the proxying of Fe, Mg or Ti ions for Al ions in octahedral positions. The interlayer positions may be occupied by any of various kinds of cations or some of them may be empty. The interlayer cations may or may not be exchangeable. It is not possible to determine base-exchange capacity or the exchangeable cations individually by calculation.

The numerical values obtained by calculation can be expressed by many different combinations of rational formulas. Therefore, the expression "end member formulas" for these minerals has no definite meaning. For a given sample, it can readily be shown that each of these combinations of formulas corresponds to the same overall chemical composition and this may closely approximate the analysis from which the formulas were calculated. But this agreement is an arithmetical necessity of the calculation, and therefore it has no significance.

The fact that the calculated negative charge on the lattice just balances the positive charge of the interlayer cations, is also an arithmetical necessity of the calculation. The balance merely indicates that no errors of calculation have been made. In no sense can it be regarded as evidence of purity of the sample. Neither can the balance be taken as evidence of the accuracy of the analysis.

Since the results of calculation on analysis of the fine grained minerals may be influenced significantly by impurities, admixed, intergrown or adsorbed, and since it may be impossible to secure definite proof that certain impurities were absent from the sample, it is suggested that the results should be treated cautiously and be given a qualitative rather than a quantitative interpretation.

INTRODUCTION

By means of calculation, several investigators (2, 8, 12, 15, 16) have attempted to determine just how the elements of certain fine grained minerals are distributed between tetrahedral, octahedral and interlayer, or so-called adsorbed, positions of the crystal lattice. In other words, the calculation is intended to show the nature of the isomorphism of the sample. The idea that these minerals belong to an isomorphous series is implicit in the assumptions on which the calculation rests.

As is well known, x-ray investigations have shown that montmorillonite and several other fine grained minerals are structurally similar to pyrophyllite and the micas. This means that they are made up of two tetrahedral planes of ions condensed with an octahedral plane, similar to that of hydrargillite or brucite, the combined three planes being considered the lattice layer. Such minerals are called three layer minerals. There is good reason for the assumption that in all these fine grained minerals, as in the silicates in general, each Si ion is surrounded by 4 O ions. From what is known about the distribution of electropositive ions in the micas, it is logical to assign Fe, Mg, and minor amounts of a few other cations to positions of octahedral coordination. On the other hand, Al ions may be either tetrahedral or octahedral, and various cations may occupy the positions formed by the hexagonal network of O ions on the surfaces of the lattice layer.

In all the better known three layer minerals, it is fairly certain that there are 8 tetrahedral, 6 octahedral, and 2 interlayer positions per lattice unit. All eight tetrahedral positions must be occupied by some electropositive ion, and all the octahedral positions may be filled, as in talc and biotite, or only 2 out of 3 positions, as in pyrophyllite and pure heptaphyllite muscovite. The interlayer positions may or may not be occupied, depending on the charges of the tetrahedral and octahedral cations.

Taking into consideration the charges of the different ions, the distribution, if accurately determined, indicates at once the centers from which the lattice charge originates. If the calculation locates the charge chiefly in octahedral positions, Marshall (12) and Ross and Hendricks (16) placed the mineral in the montmorillonite class; if in tetrahedral positions, the mineral, according to them, may be either beidellite, nontronite, or certain others.

Although neither Marshall nor Ross and Hendricks stated definitely that base-exchange capacity can be determined by calculation, it is clear from their discussion, as well as from that of Nagelschmidt (15) that they attached real significance to the fact that the calculated lattice charge balances the charges of the interlayer cations. Also, the reason why these minerals possess base-exchange property is thought to be made manifest by the calculation.

As is well known, different specimens of these minerals vary considerably in chemical composition. This has been explained on the basis of isomorphism. The problem then is to determine the distribution, in a lattice of the mica type, of the elements found by chemical analysis. This involves giving consideration to ion sizes, ion charges, and the numbers of tetrahedral, octahedral, and interlayer positions and O atoms per lattice unit.

There are several conditions that must be fulfilled before the results of the calculation can be accepted with complete confidence: (a) It must be known that the sample is composed of material of a given lattice type, (b) the purity of the sample must be assured, (c) the chemical analysis must be reasonably accurate. In addition, certain other facts must be known, as will be made clear as this discussion proceeds.

In view of the implications, as well as direct statements, in published reports on this subject, and the inherent difficulties met with in determining the purity of the fine grained minerals in general, it seemed desirable to consider rather critically (a) the effects of impurities of various kinds, and (b) the basic assumptions underlying the calculation.

TABLE 1. PERCENTAGE COMPOSITION OF SAMPLES[1]

Sample	2	3	16	M	14	R	S
SiO_2	51.29	54.60	50.64	59.47	49.4	50.30	49.56
Al_2O_3	15.53	18.17	15.73	19.11	10.2	15.96	15.08
Fe_2O_3	1.78	3.17	1.60	3.60	18.0	0.86	3.44
FeO					3.1		
TiO_2	0.23	0.13	0.08	0.66			0.40
P_2O_5				1.19			
CaO	3.24	2.49	3.34	0.21	0.6	1.24	1.08
MgO	4.34	2.02	5.37	3.51	3.5	6.53	7.84
K_2O				0.03	5.1	0.45	
Na_2O	0.35	0.15	0.25		1.4	1.19	
H_2O loss at 105°C	15.66	13.92	14.83	11.72	8.3	23.61	22.96
H_2O loss above 105°C	7.53	5.69	7.96				
Total	99.95	100.34	99.80	99.50	99.6	100.24	100.36
Exchangeable CaO	3.03	2.83	3.21	0.08[2]			

[1] Sample 2. Ca-saturated montmorillonite from bentonite, Otay, California; analyzed by J. B. Page.

Sample 3. Ca-saturated montmorillonite from bentonite, Osage, Wyoming; analyzed by J. B. Page.

Sample 16. Ca-saturated montmorillonite from bentonite, Newberry, California; analyzed by J. B. Page.

Samples 2, 3, and 16 were composed of particles 1μ or less in diameter, as measured by settling velocity.

Sample M. H-saturated montmorillonite ($<0.2\mu$) from bentonite. Reported by C. E. Marshall (12), p. 442.

Sample 14. Glauconite. Reported by Hendricks and Ross (8), p. 692.

Sample R. Montmorillonite from bentonite, Otay, California. Reported as Sample 3 by Ross and Shannon (17), p. 88.

Sample S. Montmorillonite from bentonite, Otay, California. Reported as Sample 4 by Ross and Shannon (17). Sample also contains 0.01 per cent MnO.

[2] Per cent H.

METHOD OF CALCULATION

Molal (M) values are first calculated for each electropositive ion found by analysis. The O equivalent of each is then determined by multiplying (M) Si and Ti by 2, (M) Al and Fe''' by 1.5, (M) Fe'', Ca and Mg by 1, and (M) K, Na and H ions by 0.5. The sum of the O molal values thus obtained must necessarily just equal that found by calculating the percentages of O in the several oxides shown in the analysis and then converting the sum of the O percentages into mol equivalents, as was done by Marshall (12). The ratio of 11 to the sum of the O molal values is the factor by which the molal values of the other elements are multiplied in order to convert them into atoms per 11 O atoms, the equivalent of a half lattice unit. These calculated values are then assigned to positions corresponding to those of a three layer lattice of the mica type, due consideration being given to ion sizes.

Four tetrahedral positions are filled with electropositive ions in the following order: (a) Si, (b) P, (c) Al. The remaining Al and all Fe, Ti and Mg ions are assigned to octahedral positions, provided the total does not exceed 3. If the total exceeds 3 the excess of Mg is assigned to interlayer positions along with all the remaining cations.

It may be noted here that with all the better known three layer minerals, the octahedral positions could not be occupied by cations as large as Ca, Na or K without undue distortion of the lattice, and no other positions sufficiently large for these cations are available in the interior of the lattice framework. Consequently, Ca, Na, and K ions are placed in interlayer positions, as is customary with the micas.

This method is but a slight modification of Nagelschmidt's (15) and Harvey's (6) methods. In its main outlines, it agrees also with Marshall's (12) and Hendricks and Ross' (8). In fact, all these methods are based on the same general ideas; they differ merely in the details of the calculation and the consideration given to ion size.

With all methods, it is assumed that, with minor exceptions, the analysis was made on a pure specimen, and that it was accurate. As will be shown presently, it is possible to gain some indication as to whether or not SiO_2 was present as impurity in certain samples, but this is not always possible. However, there appears to be no means of determining by calculation whether certain other kinds of impurity were present or absent.

EFFECT OF IMPURITIES

SiO_2. The effect of SiO_2 can perhaps best be shown by calculations on known mixtures of SiO_2 and theoretically pure heptaphyllite muscovite, $K(Al)_2(Si_3Al)O_{10}(OH)_2$. Such data are reported in Table 2.

Here it is shown that the calculated atoms of K and Al (both tetrahedral and octahedral) and the lattice charge,* all slowly decrease as SiO_2 is added, and the number of Si atoms gradually increases, as would be expected. However, it is necessary to add SiO_2 to the extent of about one-third of the sample in order to bring the total calculated Si atoms above 4 per half lattice unit. On the other hand, the presence of SiO_2 is at once indicated by a reduction in the number of octahedral atoms below the normal 2.0.

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* Lattice charge is determined by subtracting the sum of the charges of all tetrahedral and octahedral cations from 22, the charge of 10 O ions and 2 (OH, F) ions.

TABLE 2. EFFECT OF SiO_2 ON CALCULATED LATTICE POSITIONS FOR MUSCOVITE

Sample	Interlayer	Octahedral	Tetrahedral		Total Octahedral Atoms	Charges	
	K	Al	Si	Al		Lattice	Interlayer cations
Pure muscovite by wt.	1.000	2.000	3.000	1.000	2.000	−1.000	+1.000
1 part SiO_2 +100 parts muscovite	0.988	1.994	3.030	0.970	1.994	−0.988	+0.988
5 parts SiO_2+100 parts muscovite	0.945	1.971	3.142	0.858	1.971	−0.945	+0.945
20 parts SiO_2+100 parts muscovite	0.806	1.903	3.486	0.514	1.903	−0.805	+0.806
40 parts SiO_2+100 parts muscovite	0.675	1.837	3.813	0.187	1.837	−0.676	+0.675

If applied to analyses of similar mixtures, the calculated values shown in Table 2 might easily be interpreted as indicating a hydrous mica. Thus there is strong reason why any sample showing less than 2.0 calculated octahedral cations per half lattice unit should at once be suspected of containing SiO_2 as impurity. In fact, to accept the results on any sample of the three layer minerals when the total octahedral atoms is less than 2.0, is to open wide the door to relatively large amounts of SiO_2 as impurity.

Contrary to what is likely to be anticipated, the results of Table 2 show that the presence of SiO_2 as impurity is not necessarily reflected by an excess of calculated Si ions, but rather by a deficiency of the ions which go into octahedral positions. This is an important point to which further reference will be made. With pyrophyllite and talc, SiO_2 as impurity is at once indicated by an excess of calculated Si atoms, but this is not true of minerals which contain Al in tetrahedral coordination.

In this connection it should be pointed out that Marshall avoided a deficiency of octahedral atoms by assigning Ca atoms to this layer in numbers sufficient to provide a total of 2.0 atoms per half lattice unit. Whatever excess of Ca remained was referred to as among the "cations per unit cell," whether exchangeable or nonexchangeable. Since each half lattice unit presumably contains 3 octahedral positions, if Ca ions can fit into some of them, why not into others? In a word, if any nonexchangeable Ca ions are assigned to octahedral positions, why not all of them?

Hendricks and Ross' remarks on this point should also be noted. In commenting on the means by which they provide equivalence between the calculated charge on the lattice and that of the interlayer cations, they state: "It is brought into agreement by change of Al between octahedral and tetrahedral coordination, Σ (the total) *being finally greater or less than 2.00.** In only 2 of the 42 analyses used in this study is the value of Σ below 2 and in most of them it is slightly, but significantly above 2." Again in referring to samples which gave a total of 1.94 octahedral atoms, they state: "While this is not an impossible situation, it is indicative of an unusual condition of formation and might be the result of lattice alteration." In view of the foregoing it might also have been due to SiO_2 as impurity in the sample.

TABLE 3. EFFECT OF SiO_2 ON THE CALCULATIONS FOR MONTMORILLONITE 3

Sample	Adsorbed		Octahedral				Tetrahedral		Total Octahedral Atoms	Charges	
	Ca	Na	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.195	0.021	1.540	0.174	0.007	0.220	3.979	0.021	1.941	−0.411	+0.411
Less 6% SiO_2	0.211	0.023	1.545	0.189	0.007	0.238	3.849	0.151	1.979	−0.446	+0.445
Less 8% SiO_2	0.217	0.024	1.545	0.194	0.008	0.245	3.799	0.201	1.992	−0.462	+0.458
Less 10% SiO_2	0.224	0.024	1.547	0.200	0.008	0.253	3.748	0.252	2.008	−0.473	+0.472

TABLE 4. CALCULATIONS ON MONTMORILLONITE 16 ASSUMING VARIOUS IMPURITIES

Sample	Adsorbed		Octahedral				Tetrahedral		Total Octahedral Atoms	Charges	
	Ca	Na	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.276	0.037	1.328	0.093	0.004	0.616	3.900	0.100	2.041	−0.589	+0.589
Less 1.60% Fe_2O_3	0.279	0.037	1.396		0.005	0.624	3.950	0.050	2.025	−0.594	+0.595
Less 0.02 mols Al	0.279	0.037	1.302	0.094	0.005	0.624	3.950	0.050	2.025	−0.594	+0.595
Less 0.0167 (M) Mg	0.278	0.037	1.365	0.093	0.005	0.543	3.928	0.072	2.006	−0.592	+0.593
Less 0.0223 (M) Si + 0.0167 (M) Mg[1]	0.283	0.038	1.362	0.095	0.005	0.553	3.897	0.103	2.015	−0.606	+0.604
Less 0.01 (M) Si, 0.0067 (M) Al and 0.0167 (M) Mg[2]	0.281	0.038	1.355	0.095	0.005	0.550	3.931	0.069	2.005	−0.599	+0.600

[1] Equivalent to talc.

[2] Approximately equivalent to chlorite.

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* Italics by the writer.

Table 3 reports the calculations on a sample of montmorillonite with and without the elimination of certain amounts of SiO_2 from the analysis. The results show that, as SiO_2 was eliminated, the calculated values for all other cations gradually increased, as would be expected from the results shown in Table 2. It is necessary to eliminate SiO_2 to the extent of about 10 per cent of this sample in order to raise the total octahedral cations to 2.0. These data further confirm the idea that SiO_2 as impurity may be reflected by the number of octahedral cations rather than by an excess of tetrahedral Si ions. However, as will be shown later, this is not necessarily apparent.

Effect of Fe_2O_3 *and* Al_2O_3. As shown in Table 4, the elimination of Fe''', or an equivalent amount of Al, produces identical effects on the calculated values for all the other ions. This is merely a necessary consequence of the facts that both are trivalent and both occupy corresponding lattice positions. The amount of octahedral Fe''' and Al, being reduced by the elimination, the total octahedral cations was reduced accordingly. Thus the effect of Fe_2O_3 or Al_2O_3 as impurity is to produce changes in the calculated values exactly the opposite of those produced by SiO_2.

Effect of P_2O_5 *and* TiO_2. Marshall (12) reported analyses of samples of montmorillonite from a bentonite, which contained exceptional amounts of P_2O_5 and considerable TiO_2. He pointed out that, theoretically, P ions could occupy tetrahedral positions in the montmorillonite lattice. Neverless, montmorillonite has the power to adsorb phosphate ions from solutions, possibly by exchange with OH ions on the edges of the lattice.

As is well established, TiO_2 is often found as leucoxene in fine grained materials of volcanic origin. Moreover, Ti minerals are extremely insoluble and, therefore, it is improbable that Ti ions will become available for lattice positions during the alterations which volcanic materials must undergo in the formation of bentonite.

TABLE 5. MONTMORILLONITE M. CALCULATED LATTICE

Sample	Adsorbed			Octahedral				Tetrahedral			Total Octahedral Atoms	Charge	
	Ca	K	H	Al	Fe'''	Ti	Mg	Si	P	Al		Lattice	Interlayer cations
As analyzed	0.015	0.002	0.314	1.429	0.177	0.033	0.342	3.890	0.066	0.044	1.981	−0.344	+0.346
Less 5% SiO_2	0.015	0.002	0.334	1.425	0.188	0.035	0.363	3.789	0.070	0.141	2.011	−0.366	+0.366
Less TiO_2	0.015	0.002	0.316	1.461	0.178		0.344	3.913	0.066	0.021	1.983	−0.350	+0.348
Less P_2O_5	0.015	0.002	0.319	1.444	0.180	0.033	0.347	3.947		0.051	2.004	−0.353	+0.351
Less TiO_2 and P_2O_5	0.015	0.002	0.321	1.479	0.181		0.349	3.973		0.027	2.007	−0.355	+0.353

Hence, it is of interest to consider the effects of P_2O_5 and TiO_2 as impurities. The data presented in Table 5 illustrate this point. The analysis used was that reported by Marshall for extremely small particles ($<0.2\mu$) of montmorillonite. Larger particles from the same bentonite were also analyzed. Marshall pointed out that particles larger than 0.5μ contained an excess of SiO_2. As shown in Table 5, the particles even less than 0.2μ might also have contained SiO_2 as impurity, since the total calculated octahedral atoms of the sample as analyzed was somewhat less than 2.0. However, this might have been due to adsorbed or admixed phosphate, for the elimination of P_2O_5 affected the calculated results remarkably like the elimination of SiO_2, that is, it tended to increase the number of calculated octahedral atoms.

The same general kind of results were obtained by calculating Marshall's analysis of the sample 0.5μ–0.2μ, but with the samples coarser than 0.5μ the sum of the calculated Si and P atoms exceeded 4 per half lattice unit which, as indicated above, Marshall considers to be evidence of an excess of SiO_2.

It should be pointed out that Marshall's samples were electrodialyzed. Hence, they could hardly have contained soluble salts as impurities. What effect electrodialysis produces on adsorbed phosphate is not certain. Conceivably, it might remove the same. Hence, it is not certain that phosphate was adsorbed on this sample.

The analyses of the several sized particles as reported by Marshall indicate that this bentonite was extraordinarily heterogeneous. Silica was no doubt the most abundant impurity, but other impurities were also probably present, and, as indicated above, there is reason for doubt about the purity of even the smallest sized particles. As between particles $<0.2\mu$ and those from 0.2μ to 0.5μ, the ratios $SiO_2:Al_2O_3:Fe_2O_3:MgO$ were fairly constant, but this was far from true of the ratios $P_2O_5:CaO:TiO_2$. The writer is unable to avoid the conclusion that all these samples were more or less impure, and the same is thought to be true of samples 2, 3, 16 as reported in this paper.

Effect of Interleaving. In addition to admixtures, the crystals of these minerals might be intergrown with layers of chlorite, talc, brucite, hydrargillite, or possibly certain other minerals, as Gruner (5) suggested for vermiculite and Hendricks and Alexander (7) suggested for certain soil colloids. Therefore, it is appropriate to consider what effects would be produced by intergrowths of these substances. Such data are presented in Table 4. The effects on the calculation made on any of these samples will, of course, be the same whether the impurities were present as admixtures or were intergrown with the crystals as occasional layers.

It is of interest to note, first, that the elimination of any one of these substances, as well as of Fe_2O_3, produced one effect in common, namely a reduction in total octahedral atoms. The presence of only a very small amount of any one of these substances would account for the fact that the calculation on the original analysis gave results which indicated a certain percentage of octophyllite lattice units. (An excess above 2.0 of total calculated octahedral atoms must represent octophyllite units.) Secondly, the elimination of none of these substances greatly affected the calculated overall lattice charge. Other minor effects are apparent in the table.

Comparison of Table 4 with Tables 2 and 3 shows that the effects of SiO_2 as impurity might be largely cancelled by the presence of any one of several other kinds of impurity, whether present as admixtures or intergrown. Thus the fact that the total calculated octahedral atoms is exactly 2.0 per lattice unit is not positive proof that the sample was pure.

ADSORBED CATIONS

The foregoing calculations were made on the assumption that all the Mg, Al and Fe were present either as essential framework ions or else as constituents of some impurity. It is of interest to examine this assumption.

TABLE 6. CALCULATIONS ON DIFFERENT SAMPLES OF MONTMORILLONITE FROM THE SAME DEPOSIT OF BENTONITE

Sample	Adsorbed				Octahedral				Tetrahedral		Total Octahedral Atoms	Charge	
	Ca	K	Na	Mg	Al	Fe'''	Ti	Mg	Si	Al		Lattice	Interlayer cations
2	0.267		0.052		1.366	0.103	0.013	0.498	3.955	0.045	1.980	−0.590	+0.586
R	0.103	0.045	0.178		1.343	0.050		0.752	3.889	0.111	2.145	−0.428	+0.429
S	0.089				1.176	0.199	0.023	0.898	3.810	0.190	2.296	−0.177	+0.178
R Alternate	0.103	0.045	0.178	0.145	1.343	0.050		0.607	3.889	0.111	2.000	−0.718	+0.719
S Alternate	0.089			0.296	1.176	0.199	0.023	0.602	3.810	0.190	2.000	−0.769	+0.770

Table 6 reports the calculations on three different samples of montmorillonite, all of which were obtained from the same deposit of bentonite at Otay, California. Reference to Table 1 shows that the chief differences between these samples were in their Fe_2O_3 content and in the ratio of CaO to MgO. The fact that sample 2 contained much more CaO and correspondingly less MgO than samples R and S (17) was probably due chiefly to differences in the preliminary treatment of the samples. Number 2 was intentionally treated in such way as to bring about as complete

Ca saturation at *pH* 7 as possible, which means that readily exchangeable cations of all kinds were replaced by Ca ions. Soluble salts were also carefully removed. As separated from the original bentonite, sample 2 contained a substantial amount of exchangeable Mg. It is probable that samples R and S also contained exchangeable Mg. Attention is also called to the fact that K_2O and Na_2O were reported in sample R but not in sample S. In making the calculations on sample S, Mn was left out because the amount present would not affect the calculations significantly.

Mg Ions. The calculated values for samples R and S are reported on two bases, namely, (a) with all Mg ions in octahedral coordination, and (b) with a part of the Mg ions in interlayer or adsorbed positions. Since no information is available concerning the actual content of exchangeable Mg in these two samples, the assignment of Mg ions to adsorbed positions was purely arbitrary, as it must necessarily be with any sample whose content of exchangeable Mg is unknown. Conversely, *the assignment of all Mg ions to octahedral positions where the content of adsorbed Mg is unknown is almost equally arbitrary.* If we assume that all the Mg ions were in octahedral coordination in these two samples, then the lattice charge per half lattice unit would be -0.428 and -0.177, respectively, whereas, if amounts of Mg were adsorbed sufficient to provide exactly 2.0 octahedral cations, the respective charges would be -0.718 and -0.769. Thus we see that the position to which Mg is assigned may make great differences in the distribution of the charges.

Unfortunately, we have no accurate analytical method for differentiating sharply between exchangeable Mg ions and Mg ions located in octahedral positions. For example, when a finely pulverized sample of biotite is treated with a salt solution, as in the determination of the exchangeable bases, considerable Mg passes into solution. Kelley and Jenny (10) suggested that this is evidence of the partial decomposition of biotite. In addition, after as complete replacement as possible by Ca ions of all exchangeable cations held by montmorillonite, further treatment of the sample with ammonium salt solution commonly brings Mg into solution for a prolonged period. Moreover, upon electrodialyzing montmorillonite, Mg passes into the cathode cell of the apparatus for an indefinite period.

Therefore, it is not possible to draw a sharp line between interlayer Mg and octahedral Mg. Nevertheless, there is good evidence that many clays contain exchangeable Mg. Soil colloids commonly contain substantial amounts. As shown by Kelley and Liebig (11), treatment of montmorillonite with sea water results in the taking up of considerable Mg by exchange. Since the bentonites have probably been formed in saline solutions which contained more or less Mg, it is therefore to be expected that montmorillonite from bentonite will contain more or less adsorbed Mg.

Although mica with Mg ions in interlayer positions is not definitely known, it is not certain that nonexchangeable but adsorbed Mg could not occur in the three layer minerals just as Ca, Na and K are known to occur in the micas.

Fe and Al Ions. It is apparent that the differences in Fe_2O_3 in these samples of montmorillonite from Otay, California, are reflected in the calculated values as shown in Table 6. Even granting that the K_2O, Na_2O and TiO_2 found by analysis were present as impurities (for which substantial proof is entirely lacking) these samples still differ considerably.

As is well known, indefinite, but usually positive, amounts of Al, Fe and frequently Mn are brought into solution upon treating many samples and types of clay from different localities with neutral salt solutions. This is often explained on the ground that these cations were present in exchangeable form, that is adsorbed. As Marshall pointed out, the amount of such Al may equal one or two per cent of the sample. Since exchangeable monovalent and divalent cations can be readily replaced by trivalent cations by treating the sample with a dilute solution of $AlCl_3$ or $FeCl_3$, there seems to be no necessary reason why natural deposits of montmorillonite might not contain at least small amounts of adsorbed Al and Fe ions. These might be adsorbed not as trivalent ions but as divalent or monovalent ions. Hence, it is pertinent to consider the effect of adsorbed Al and Fe on these calculations.

In all the preceding calculations none of the Al or Fe was assigned to adsorbed positions. However, if any part of these elements should have been adsorbed, the effect on the calculated formula would have been quite analogous to what has already been shown for Mg ions. That is, the total octahedral atoms would be decreased and the lattice charge and that of the adsorbed cations would be increased. Hence, it is important to know definitely what part, if any, of the Al and Fe of the sample is adsorbed. Unfortunately, we have no accurate method for this determination. Mattson (14) found upon treating certain montmorillonitic soil colloids with $AlCl_3$ that substantial amounts of Al were adsorbed and at the same time the base exchange capacity decreased markedly. This latter might mean that adsorbed Al ions do not dissociate readily. Nevertheless, it is improbable that any considerable amount of Al or Fe ions will be adsorbed on the naturally occurring montmorillonite of strongly alkaline deposits.

H Ions. As is well known, the exchangeable metallic cations of colloids can be readily replaced by H ions. Any sample of montmorillonite which has been subjected to the sustained leaching action of rain water is likely to contain more or less adsorbed H ions. Certain deposits of bentonite are definitely acidic and the montmorillonite of these almost certainly contains adsorbed H ions and possibly adsorbed Al ions also. Other deposits are either approximately neutral or slightly alkaline. These may also contain more or less adsorbed H ions. It is important to stress here that the fact that the material is neutral or even slightly alkaline, does not necessarily preclude the possibility of adsorbed H ions. If present, adsorbed H ions certainly would serve to neutralize negative charges on the lattice, and to ignore the same would alter all the calculated values, since the O equivalent of the adsorbed H ions would be left out. Just as in the case of Al and Fe, we have no certain method of determining adsorbed H ions except by treating the sample with fairly strongly alkaline solutions. However, under the alkaline conditions of many bentonite deposits, it is unlikely that important amounts of adsorbed H ions are present.

GLAUCONITE

Table 7 reports the calculations on a sample of glauconite, the analysis of which was reported by Hendricks and Ross (8). These data show that the results of calculation on glauconite would be influenced by impurities very much as are those of montmorillonite. By assuming the presence of 1.60 per cent Fe_2O_3, or one layer of brucite or chlorite per 50, an equally possible lattice can be calculated for this sample. Calculations based on an assumed mixture of 1 part CaO and 100 parts of this sample as analyzed also gave a perfectly stable lattice. Thus it is shown that more than 1 per cent of $CaCO_3$ might be present in material of this kind with-

TABLE 7. GLAUCONITE 14. CALCULATED LATTICE

Sample	Adsorbed			Octahedral				Tetrahedral		Total Octahedral Atoms	Charge	
	Ca	K	Na	Al	Fe‴	Fe″	Mg	Si	Al		Lattice	Interlayer cations
As analyzed	0.048	0.476	0.198	0.499	0.991	0.189	0.382	3.618	0.382	2.061	−0.770	+0.770
Less 1.60% Fe_2O_3	0.048	0.482	0.201	0.553	0.915	0.192	0.386	3.662	0.338	2.046	−0.778	+0.778
Less 0.0167 (M) Mg	0.047	0.480	0.200	0.528	0.998	0.191	0.311	3.642	0.358	2.028	−0.776	+0.774
Less 0.01 (M) Si, 0.0067 (M) Al, and 0.0167 (M) Mg[1]	0.048	0.485	0.203	0.509	1.011	0.193	0.314	3.642	0.358	2.027	−0.784	+0.784
Plus 1 part CaO per 100	0.124	0.472	0.197	0.459	0.983	0.208	0.379	3.586	0.414	2.029	−0.914	+0.917

[1] Approximately equivalent to chlorite.

out its presence being revealed by the calculation. The effects produced by adding CaO assume special interest in the light of the fact that Hendricks and Ross calculated formulas for certain samples of glauconite which contained substantial amounts of CO_2.

The foregoing data show the general types of effects that would be produced by various kinds of impurities. If the amount of certain impurities exceeds a certain percentage, which percentage depends on the composition of the sample, an excess of SiO_2 will be found, or the total octahedral ions will be insufficient to provide a structurally stable lattice, or the sum of the adsorbed cations per half lattice unit will exceed 1. But within limits wide enough to embrace substantial amounts of impurities, it is quite possible to calculate lattices which theoretically would be perfectly stable. If mixtures of these kinds should be analyzed in the first place, none of these methods of calculation apparently affords a certain means of detecting the same. Moreover, the calculation cannot be used as a check on the accuracy of the analysis. In fact, theoretically possible lattices can be calculated on the basis of grossly inaccurate analyses.

It should be pointed out here that neither Marshall nor Hendricks and Ross employed lattice calculations as a means of establishing the purity of their samples. Nevertheless, the fact that definite places in the lattice were found for every element and definite formulas were proposed for certain samples, implies that the samples were thought to be pure, and it is certain that other scientists have assumed that this was evidence of purity.

Pyrophyllite Mixture

To show further that these calculations could lead to erroneous conclusions, not only as to the purity of the sample, but also as to the specific mineral present, the following calculations were made. The percentage composition of theoretically pure pyrophyllite was calculated. Then the percentage composition of a hypothetical mixture consisting of 100 parts pyrophyllite, 5 parts MgO, and 2.5 parts of CaO was calculated. Applying to this hypothetical analysis the same kind of calculations used above, results were obtained as reported in Table 8. These data show not only a

Table 8. Hypothetical Mixture of Pyrophyllite, MgO, and CaO
Calculated Lattice

Adsorbed	Octahedral		Tetrahedral		Total Octahedral Atoms	Charges	
Ca	Al	Mg	Si	Al		Lattice	Interlayer cations
0.152	1.686	0.423	3.791	0.209	2.109	−0.305	+0.304

theoretically possible lattice with all the Ca as adsorbed ions, and all the Mg in octahedral coordination, but they also indicate that the analysis was that of a Ca-saturated montmorillonite or glauconite. An equally plausible lattice can be shown for this mixture by transferring Mg from octahedral to absorbed positions.

While, of course, no competent mineralogist is likely to mistake such a mixture for montmorillonite, these results show something of the treachery of this kind of calculation, particularly when applied to analyses taken from the literature.

END MEMBERS

Rational formulas corresponding to the preceding lattice values can readily be derived. Various combinations of theoretically possible formulas can be shown to be possible for a given sample. Four different combinations are given in Table 9 for the foregoing sample of glauconite. Many more could be shown. However, there are certain limits that cannot be exceeded. For example, the calculation definitely fixes the number of half lattice units containing tetrahedral Al at 38.5 per cent of the total in this sample, and the number containing 3 octahedral atoms must be 6.1 per cent. The latter may have been either neutral or charged, but since only divalent cations can occupy 3 octahedral positions in a given half lattice unit without imparting a positive charge to the octahedral layer, this may possibly impose a limit on the choice. In other respects rather wide choice is permissible. If this sample was a pure specimen, 23 per cent of the lattice units must have been electrically neutral, that is, they contained no interlayer cations.

Thus it follows that, insofar as this sample is concerned, the expression "end members," is essentially meaningless. This conclusion is consistent with Bragg's (1) view of the micas. He stated (p. 213): "It is almost impossible to give formulas of end members when so many types of replacement may take place. Mauguin's work showed that the concept of end members must be replaced by that of the number of atoms in certain groups within the cell. . . . The main point brought out by Mauguin's analysis is that the total number of oxygen atoms in the structural unit (in fluoriferous micas, of O and F atoms) is always *twelve* within the errors of analysis. Other constituents vary widely but this remains constant."

If the sample as analyzed was pure, it necessarily follows that the various kinds of lattice units were randomly distributed in all the small crystals present in this sample. Although K ions were the most abundant interlayer cations, about $\frac{1}{4}$ were Na ions with a still smaller number of Ca ions. How were these distributed and were they exchangeable?

TABLE 9. COMBINATIONS OF FORMULAS DERIVED FROM CALCULATED DATA FOR GLAUCONITE 14, TABLE 7

Per cent		I	Per cent		II
6.1	23.0	$(Mg)_3(Si)_4O_{10}(OH)_2$	6.1	23.0	$(Mg)_3(Si)_4O_{10}(OH)_2$
16.8		$(Fe''')_2(Si)_4O_{10}(OH)_2$	1.9		$(Fe''')_2(Si)_4O_{10}(OH)_2$
0.1		$(Al\ Fe''')(Si)_4O_{10}(OH)_2$	15.0		$(Al)_2(Si)_4O_{10}(OH)_2$
18.9	77.0	*$x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$	18.9	77.0	$x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$
19.9		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$	19.9		$x(Al\ Mg)(Si)_4O_{10}(OH)_2$
13.3		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$	38.2		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$
24.9		$x(Al)_2(Si_3Al)O_{10}(OH)_2$	100.0		
100.0					
		III			IV
7.5	23.0	$(Fe''')_2(Si)_4O_{10}(OH)_2$	22.9	23.0	$(Fe''')_2(Si)_4O_{10}(OH)_2$
15.5		$(Al)_2(Si)_4O_{10}(OH)_2$	0.1		$(Al\ Fe''')(Si)_4O_{10}(OH)_2$
6.1	77.0	$x(Mg)_3(Si_3Al)O_{10}(OH)_2$	6.1	77.0	$x(Fe'')_3(Si_3Al)O_{10}(OH)_2$
32.1		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$	7.2		$x(Fe''')_2(Si_3Al)O_{10}(OH)_2$
19.9		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$	24.9		$x(Al)_2(Si_3Al)O_{10}(OH)_2$
18.9		$x(Al\ Fe'')(Si)_4O_{10}(OH)_2$	38.2		$x(Fe'''Mg)(Si)_4O_{10}(OH)_2$
100.0			6.0		$x(Fe'''Fe'')(Si)_4O_{10}(OH)_2$
			100.0		
As Analyzed			As calculated from any set of the above formulas		
SiO_2	49.4		SiO_2	51.81	
Al_2O_3	10.2		Al_2O_3	10.70	
Fe_2O_3	18.0		Fe_2O_3	18.86	
FeO	3.1		FeO	3.24	
CaO	0.6		CaO	0.61	
MgO	3.5		MgO	3.67	
K_2O	5.1		K_2O	5.34	
Na_2O	1.4		Na_2O	1.46	
H_2O	8.3		H_2O	4.29	
Total	99.6		Total	99.98	

* x = Ca, 4.8; K, 47.6; Na, 19.8.

Socalled end members were also figured out for montmorillonite 16. Just as with the sample of glauconite, a considerable number of combinations of formulas is possible. With this sample, Ca ions were known to be the only exchangeable cations present, but the sample also contained nonexchangeable Ca and nonexchangeable Na. The last-named Ca ions might have been present as constituents of a substance corresponding to the brittle mica, margarite, and the Na ions as soda mica. Were these arranged randomly or in occasional layers? If the latter, then the crystals were interstratified, and hence not homogeneous. Thus it becomes apparent that various complications and essentially unanswerable questions arise when this question is examined closely.

Each combination of formulas listed in Table 9 contains every element found by analysis exclusive of H_2O. In the lower part of the table the original analysis of the sample and the chemical composition calculated from one of the combinations of formulas are shown. Each combination of formulas gives the same chemical composition. It will be noted that the calculated composition approximates the analysis. However, they differ somewhat. This is due mainly to differences in H_2O, but partly to the fact that the original total was 99.6 instead of 100. However, the ratio of $SiO_2 : Al_2O_3 : Fe_2O_3$, etc., is the same in both. If no errors of calculation have been made, this must be so, since the ratio of element to element is preserved throughout the calculation. Therefore, the fact that the calculated chemical composition approximates the original analysis has no significance; it is merely an arithmetical necessity and means nothing more than that no errors of calculation have been made.

It is also quite possible to derive rational formulas for known mixtures, such as the pyrophyllite mixture shown in Table 8. In fact, the calculated values, as listed in the foregoing tables, represent a sort of average formula for each sample. The rational formulas merely express the same results in terms of whole rather than fractional atoms. Therefore, the fact that rational formulas can be derived and that the calculated chemical composition approximates the analysis cannot in any sense be regarded as evidence of purity. Nor does it have any other significance.

That the calculated per cent of H_2O differs from the percentage found by analysis, might, of course, mean that the sample contained adsorbed H_2O. On the other hand, it might also mean that the sample contained some constituent, either admixed or intergrown, with a greater content of OH ions. These results suggest that exact knowledge as to the lattice OH ions of the sample could be used as a check on purity. Ross and Hendricks (16) pointed out that thermal analysis shows "that H_2O lost above 350°C is usually a close measure of the hydroxyl content." On the other hand, considerable variation has been found in the weight losses when samples of montmorillonite from different sources are heated from 300°C or even 400°C to 800°C. Furthermore, the temperature range over which adsorbed H_2O is driven off overlaps that of H_2O loss from lattice OH ions, as was reported by Kelley, Jenny and Brown (9). For this reason, thermal analysis is not an accurate means of determining lattice OH ions. As is well established, the socalled $+H_2O$ of montmorillonite from different sources often differs substantially. With samples 2, 3 and 16, Table 1, all of which were Ca-saturated, the H_2O given off above 105°C varied from 5.69 to 7.96 per cent.

General Discussion

Among the impurities most likely to be found in the fine grained minerals, SiO_2 is perhaps the most important. It may be present as crystalline quartz or cristobalite, as amorphous SiO_2, or as adsorbed silicate ions. *X*-ray analysis and optical methods can probably be depended on for evidence concerning crystalline forms of SiO_2, at least if the amount exceeds a low minimum, but amorphous SiO_2 and adsorbed silicate ions are more difficult to detect. That silicate ions are likely to be adsorbed by montmorillonite is suggested by the following. Bentonite deposits, the most abundant source of montmorillonite, are often alkaline, sometimes strongly so, as is the case with the Wyoming deposit from which sample No. 3 was obtained. This is just the condition in which SiO_2 is soluble. It is well established that upon treating a sample of montmorillonite with a soluble silicate, substantial amounts of silicate ions become adsorbed, possibly through exchange with OH ions on the edges of the lattice. Phosphate ions might also be similarly adsorbed. Such adsorbed ions are held rather tenaciously, and when present they will, of course, influence the total SiO_2 and P_2O_5 of the sample.

Amorphous Fe or Al oxide or hydroxide may also be present, although the amount in carefully prepared samples is not likely to be great.

As indicated already, interleaving is a possibility. Hydrargillite, chlorite, brucite, talc, pyrophyllite, the micas, kaolinite, and possibly other minerals might be present as occasional layers in the crystals of montmorillonite and other fine grained minerals. But whether the sample contains adsorbed, admixed or intergrown constituents, the effect on the calculations would be the same. If any of these kinds of substances is present in any of these forms, the crystals could not be said to be homogeneous.

Since montmorillonite has an expanding lattice, it would be expected that all the interlayer cations would be exchangeable, but many samples are known to contain small amounts of nonexchangeable Ca, Na and K. However, if the sample should contain an occasional layer with the composition of margarite, soda mica, muscovite or biotite, the adsorbed cations attached to these layers would probably not be exchangeable. The attractions of such interlayer cations might be shared between adjacent layers and thus prevent expansion along these interlattice planes. It is probable that such layers in materials like the fine grained minerals could not be detected on an ordinary *x*-ray powder diagram, by optical means or by thermal analysis. Interleaving would certainly have a bearing on the chemical composition, the calculated octahedral atoms, and the fact that nonexchangeable cations were present.

As pointed out already, Marshall (12) assigned Ca ions to octahedral positions and Caldwell and Marshall (2) assigned only exchangeable ions to interlayer positions. Accordingly, nonexchangeable Ca and K ions were placed in the gibbsite or brucite sheets of the lattice, that is in octahedral positions. In the opinion of the writer, this is very questionable. These ions are too large to occupy such positions and to assign them to octahedral positions makes it possible to calculate lattices for grossly impure samples, such as soil colloids almost certainly are.

The importance of definite information as to what ions are adsorbed can scarcely be overemphasized. This may apply to Si, P, Al, and Fe, but perhaps more particularly to Mg and H ions. Montmorillonite from certain bentonites is known to contain considerable replaceable Mg. It is not safe to assume, in the absence of evidence to the contrary, that all Mg ions occupy positions of octahedral coordination. Whether or not all interlayer Mg ions are readily exchangeable is not known definitely.

As indicated already, adsorbed H ions may not be completely exchangeable at *pH* 7. Apparently complete dissociation of all adsorbed H ions takes place only at relatively high *pH*. It has been found that montmorillonite is able to neutralize $Ca(OH)_2$ or $Ba(OH)_2$ at relatively high *pH* values. At the same time Ca or Ba ions become adsorbed. Therefore, the term "base saturation" can be defined only in terms of *pH*. It follows that the determination of adsorbed H ions involves considerable uncertainty. The same can be said, even more emphatically about the determination of adsorbed Al ions. We simply have no certain method for this determination. Therefore, it is difficult to distinguish sharply between Al as framework cations and as interlayer cations.

As shown in Table 6, different samples of montmorillonite from one and the same bentonite deposit may vary considerably in chemical composition. This variation is not confined to SiO_2 and the usual adsorbed cations; it also applies to Fe''' as well. This is difficult to harmonize with the idea that the samples were composed exclusively of one homogeneous mineral. Critical study is needed of different samples carefully selected from the same stratum and from different strata of a given deposit.

Reference has been made to the fact that Marshall's samples were electrodialyzed. While electrodialysis unquestionably has usefulness in the study of the clay minerals, it is very questionable when applied to substances to be used for lattice calculation. The reason is that under electrodialysis decomposition gradually takes place and the decomposition products are not dialyzed out at equal rates. Mattson (13) showed that the electrodialyzing material adjacent to the anode membrane may have different composition from that adjacent to the cathode membrane. Caldwell and Marshall found that the decomposition products pass through the membranes at widely different rates. The Hector clay underwent decomposition to an extreme degree.

The foregoing tables show that the calculated charge on the lattice is just balanced by that of the interlayer or socalled adsorbed cations. This was true in all cases, and the balance is not disturbed by eliminating any constituent whatever, by adding a foreign substance, or by the decision as to whether a given ion is located in framework or interlayer positions. Neither does balance depend on the accuracy of the analysis. The reason for this is found in the arithmetical necessities of the calculation itself. Since the ratios of the several electropositive ions to their O equivalents are preserved throughout the calculation, and the same ratios obtain in the substituted positions in the lattice, it is an arithmetical necessity that the sum of the charges of the electropositive ions will just equal the charges of the O ions. Therefore, the overall assemblage of ions, including O and OH ions, will be electrically neutral. If all cations are placed in framework positions of the lattice, irrespective of the size and charge of the individual ions, it will be electrically neutral, and if some of the cation are placed in interlayer positions, their total charge must necessarily just balance the charge on the lattice. The magnitude of the two respective charges will be affected by transfer of cations from interior to exterior positions, but the balance will not be affected. Hence we can say definitely that there is absolutely no significance to this balance. It merely shows that no arithmetical errors have been made in the calculation. This applies to the method of Marshall, Hendricks and Ross, and all others.*

A further consequence follows from the foregoing, namely, it is not possible to calculate base-exchange capacity from the chemical analysis. Neither is it possible to determine by calculation which ions are exchangeable and which are not. Consideration of ion sizes leads to the conclusion that certain kinds of ions must be on the exterior of the lattice layers, but this by no means proves that all of the interlayer cations are exchangeable, or that others could not be adsorbed. For example, while Mg ions can readily fit into octahedral positions, they can also, in fact sometimes actually do occur as exchangeable Mg ions, and could then not be wholly in octahedral positions. There is no known method of determining what ions are exchangeable or the base-exchange capacity save by actual experiment.

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* In recent correspondence both Marshall and Ross stated that they recognize that there is no significance to this balance. Ross also pointed out that the total octahedral atoms should be at least 2 per half lattice unit.

It should be emphasized that the actual, as contrasted with the assumed, interlayer or socalled adsorbed cations must be known before high confidence can be placed in the results of lattice calculation. Since among the various samples which have been used by previous investigators for these calculations, the exchangeable cations have been determined in only a relatively few, and since many analyses were taken from published reports which gave no information concerning their adsorbed cations, the proposed formulas cannot be said to be well established. They simply rest on too many assumptions.

However, the idea of isomorphism in the fine grained minerals is not weakened by the foregoing data and discussion; it is only the quantitative aspects thereof that are brought into question. Qualitatively, no evidence whatever has been presented that isomorphism is not a real feature of these minerals. But it is necessary to have quantitatively accurate data on which to extablish a formula. As Ross and Hendricks (16) pointed out, isomorphism affords a logical explanation for the colloidal and base-exchange properties of the minerals. No other hypothesis yet proposed so well accounts for these properties.

However, it cannot be said that this hypothesis is fully in harmony with all the facts. While the charge on the lattice, occasioned by the lack of balance between the framework cations and the electronegative O and OH ions, is probably largely responsible for the fact that montmorillonite contains exchangeable cations, the extraordinary swelling properties of the Wyoming type of bentonite and the electron micrographs of the same suggest that other factors may also be involved.

If silicate ions should be adsorbed by montmorillonite, these might be either monovalent or polyvalent, and the base-exchange capacity of the material might be increased by this adsorption. If so the exchangeable bases would then not necessarily be located between lattice layers. This, of course, is purely speculative. It suggests the need for a study on the relation between base-exchange capacity and adsorption of silicate ions.

In view of the way the results of calculation are affected by certain kinds of impurities, it is possible that montmorillonite is purely heptaphyllitic, the amount of calculated octahedral atoms in excess of 2.0 being due to interleaving. However, it will probably be difficult either to prove or disprove this idea. The author fully recognizes that isomorphism as between heptaphyllite and octophyllite is a distinct possibility, but since the calculated octahedral atoms rarely exceed 2.0 by more than one or two tenths, it seems more reasonable to assume interleaving. The same conclusions would also apply to glauconite. Ross and Hendricks' (16) formula, $Na_{0.33}$ $(Al_{1.67}$ $Mg_{0.33})(Si_4)0_{10}(OH)_2$ for montmorillonite is in agreement with the idea that this mineral is a pure heptaphyllite.

As was indicated in the introduction to this paper, Marshall and Ross and Hendricks separated beidellite from montmorillonite on the basis of the ratio of the charge on the octahedral layer to that of the tetrahedral layer. As shown in Table 3 this ratio may be influenced considerably by the presence of SiO_2 as impurity. With sample 3 as analyzed, this ratio was about 10:1, whereas, the elimination of an amount of SiO_2 sufficient to provide 2.0 octahedral atoms per half lattice unit changed this ratio to about 1:1. This, of course, does not disprove that beidellite differs from montmorillonite in the way indicated, but it does suggest that samples of alleged beidellite should be carefully scrutinized with respect to impurities of all types. As bearing on this point as well as on interleaving in general, Grim and Rowland (4) state: "The thermal evidence indicates that many bentonites and other clays thought to be composed of a single clay mineral are actually mixtures of clay minerals probably closely intergrown."

It is scarcely necessary to say that the eliminations reported in the foregoing tables were *solely* for the purpose of showing how impurities would affect the calculated results. When calculating a formula for an actual sample, it is probably rarely justifiable to eliminate any constitutent. Unless positive evidence is at hand showing that a given kind of impurity was actually present in the sample, to neglect this or that constituent, as has been done by certain workers (8, 16) is purely arbitrary and can no more be justified than the elimination of any other constituent. K_2O and Na_2O, for example, could not exist as such in natural deposits of montmorillonite or glauconite. They must be combined either as soluble salts or as some alumino or ferrosilicate. Therefore, in the absence of Cl, SO_4, etc., if these cations are eliminated, corresponding amounts of Si and Al must also be subtracted, but to do this leads at once into pure speculation. However strong the evidence of interleaving may be, if the specific substance involved is unknown, there seems to be no satisfactory correction that can be introduced in the calculation.

As is well known, F ions frequently proxy for OH ions in the micas. Consequently, the content of OH ions is complementary to that of F ions. In some samples practically all OH ions are replaced by F ions. Several workers have reported F in the highly magnesian clay which Foshag and

Woodford (3) described from Hector, California. It is probable that careful analysis will reveal the presence of F in other clays. Hence, it is pertinent to consider the effects produced on the lattice calculations by F. All the aforementioned methods are based, essentially, on the assumption that each half lattice unit contains 10 O ions and 2 OH ions or 11 O atoms in the dehydrated material. When F is a constituent of the lattice, the dehydrated form will not contain exactly 11 O atoms.

The effect of F can perhaps be best brought out by considering the following theoretical formulas for muscovite, representing the greatest possible extremes in F content:

(a) $K(Al)_2(Si_3Al)O_{10}(OH)_2$
(b) $K(Al)_2(Si_3Al)O_{10}F_2$

Mere inspection shows that the proxying of F for OH does not alter the relations of other ions. The sum of the charges of K, Al and Si ions in each formula is 22, the equivalent of 11 O ions. The presence of F in the sample will, of course, modify the absolute percentages of SiO_2, Al_2O_3, etc., but the sum of the O equivalent of all the cations just equals the O+F ions present. The ratios of Si:Al:K is the same regardless of the F content and these ratios rather than the absolute percentages determine the calculated results. Therefore, the F content should be ignored in making the calculation. To subtract an amount of O equivalent to F, as was done by Caldwell and Marshall (2), results in erroneous values for every electropositive ion present.

Finally, it is generally admitted that montmorillonite and other fine grained minerals are among the most difficult with which the mineralogist has to deal. The growing importance now being attached to these minerals and the difficulties involved in their elucidation require the application of all possible methods of investigation and the best efforts of trained workers in this field. Nothing in the foregoing should be construed as indicating that these minerals are hopelessly complex, or as casting doubt on the possibility of arriving at a satisfactory understanding of the same through investigation. The whole purpose of this paper is to show some of the difficulties that must be overcome. Only by recognizing difficulties are they likely to be overcome.

Neither should it be assumed that lattice calculation is entirely useless. Undoubtedly, these calculations have already served to show at least one reason why montmorillonite has base-exchange property, and the calculations have contributed to a better understanding of why different samples differ in percentage composition. Nevertheless, the foregoing shows that the very nature of these materials places a limit on what can be accomplished by calculation. Its value depends on the purity of the sample. Supplemental to careful selection, the sample should be rigorously tested optically, *x*-rayed, and thermo-analyzed. In addition, examination with the electron microscope may be useful, and certainly careful chemical tests including base-exchange determinations are indispensable. After all these tests have been applied, a considerable margin of doubt may still remain. The chemical analysis may even then be susceptible of different interpretation. Therefore, in the opinion of the writer, the calculated values should be treated tentatively and be given a qualitative rather than a quantitative interpretation.

Conclusions

1. Theoretically possible lattices can be calculated from analyses of grossly impure specimens of minerals. In fact, possible lattices can be calculated for mixtures of wholly amorphous substances. Therefore, three consequences follow: (a) except in extreme cases, it is not possible to determine by calculation whether or not a sample is pure; (b) theoretically possible lattices can be calculated on the basis of highly inaccurate analyses; (c) unless definite information is available showing that the sample contains crystalline material of a given type, the calculation has no value.

2. If the total octahedral atoms, as calculated, are found to be less than 2.0 per half lattice unit, the sample probably contained either SiO_2 or P_2O_5 as impurity. If the total exceeds 2.0 by one or two tenths, it is possible that Al, Fe or Mg was present either as a constituent of some impurity, admixed or intergrown, or as adsorbed cations. However, since SiO_2 tends to decrease the calculated values, while Al, Fe and Mg increase the same, the sample might contain impurities even when the total is exactly 2.0.

3. The fact that the Si atoms, as calculated, do not exceed the total number of tetrahedral positions of the three layer minerals, is not proof that the sample was free from SiO_2 as impurity. With minerals which contain tetrahedral Al ions, an excess of SiO_2 manifests itself first by a reduction in the calculated octahedral atoms and only when the amount of SiO_2 is relatively great will an excess of Si atoms be indicated.

4. Unless it is known definitely that the sample contains no appreciable amount of adsorbed Mg, the assignment of all the Mg ions to octahedral positions is arbitrary, and may lead to erroneous conclusions regarding lattice charge, adsorbed cations and chemical formula.

5. Interleaving is a possibility in all the fine grained minerals. Since small amounts of nonexchangeable Ca, Na and K are often found in

samples of montmorillonite, it is suggested that these ions may be adsorbed on distinct layers of brittle mica, soda mica, muscovite or biotite.

6. Montmorillonite and other fine grained minerals may contain adsorbed H, Al or Fe ions, but the amount is not likely to be important in strongly alkaline deposits.

7. It can readily be shown that a considerable number and variety of combinations of formulas apply equally well to a given sample. Therefore the expression, "end members," as applied to the isomorphous minerals dealt with in this paper, is essentially meaningless. That the chemical composition, as calculated from the derived formulas, approximates the original analysis, has no significance.

8. The fact that the calculated lattice charge balances the charge of the interlayer cations has no significance. Like the agreement just referred to, it is an arithmetical necessity of the calculation itself and merely shows that no errors have been made in the calculation.

9. Base-exchange capacity or the individual exchangeable cations cannot be determined by calculation, not even when the sample is absolutely pure.

10. It is highly probable that the fine grained three layer minerals belong to isomorphous series, but the quantitative aspects of isomorphism can be determined by calculation only if the sample is free from important amounts of impurities, both admixed and intergrown, and at the same time all adsorbed ions are known.

11. There is absolutely no substitute for purity if reliable formulas are to be calculated.

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VARIATIONS IN COMPOSITION AND PROPERTIES OF THE CALCIFEROUS AMPHIBOLES

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ABSTRACT

By plotting the position of about two hundred analyses of common hornblende analyses on a (partial) triangle with $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$, $Ca_2(Mg, Fe)_3(Al, Fe)_4Si_6O_{22}(OH)_2$, $NaCa_2(Mg, Fe)_5AlSi_7O_{22}(OH)_2$, and $NaCa_2(Mg, Fe)_4(Al, Fe)_3Si_6O_{22}(OH)_2$ as its end-members, Hallimond has shown very clearly that many hornblendes have a composition which can be expressed in terms of these four formulas. By using this (partial) triangle as the base of a (partial) triangular prism it is possible to represent (in a three dimensional figure) all the most important variables in the composition of hornblende, and this makes it possible to show the relations between variations in composition and in physical properties as done in Fig. 9. Since several (less important) variables are disregarded in developing this diagram it must be considered as only an approximation. The formulas used in this figure are:

$Ca_2Mg_5Si_8O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$

$Ca_2Fe_5Si_8O_{22}(OH)_2$
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$
$NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$

The position of any hornblende analysis in this (partial) triangular prism can be obtained by calculating the number of each kind of atom for 2400 $(O+OH+F)$, dividing each side of the triangle into 200 parts, and then using Si atoms -600 as one coordinate, $Ca+Na+K-200$ as a second coordinate and $200(Mg+Al)$ divided by $Mg+Al'+Fe''+Fe'''+Ti+Mn$ as the third (vertical) coordinate (Al' being equal to total Al atoms minus Al atoms necessary to make $Si+Al$ equal to 800).

In a very similar way the composition of certain oxyhornblendes is shown in Fig. 10 and the relations between composition and optical properties are shown in Fig. 12, using the following formulas for the ferriferous end-members:

$Ca_2Fe''_3Fe'''_2Si_8O_{24}$
$NaCa_2Fe''_3Fe'''_2AlSi_7O_{24}$

$Ca_2Fe''Fe'''_4Al_2Si_6O_{24}$
$NaCa_2Fe''_2Fe'''_3Al_2Si_6O_{24}$

This diagram is based on very incomplete data and should be used with caution.

For a long time the writer has emphasized the fact that many minerals vary considerably in composition and he has published diagrams showing the relations between variations in composition and corresponding variations in physical properties for most of the common minerals. In this work hornblende has been exceptionally difficult to deal with, first, because its composition was not fully understood, and second, because it varies in composition in so many ways that no ordinary diagram can be used to represent these variations.

Under these circumstances Hallimond's excellent study of the calciferous amphiboles[1] is of great assistance. It should be clearly understood that Hallimond's study does not include all the possible variations in composition in amphibole nor even all those for which there is now good evidence of continuous variation. But it does include all the commonest variables and therefore includes most of the "common hornblendes" as well as ordinary tremolite, actinolite, ferrotremolite, pargasite, and hastingsite.

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[1] Hallimond, A. F., *Am. Mineral.*, **28**, 65 (1943).

Hallimond includes oxyhornblendes ("basaltic hornblendes") in his study. However, the optic properties of oxyhornblende differ so much from those of common hornblende that it is necessary to deal with them separately for the purposes of the present study. Moreover, oxyhornblendes differ also in composition from common hornblendes. It is desirable to begin with common hornblendes.

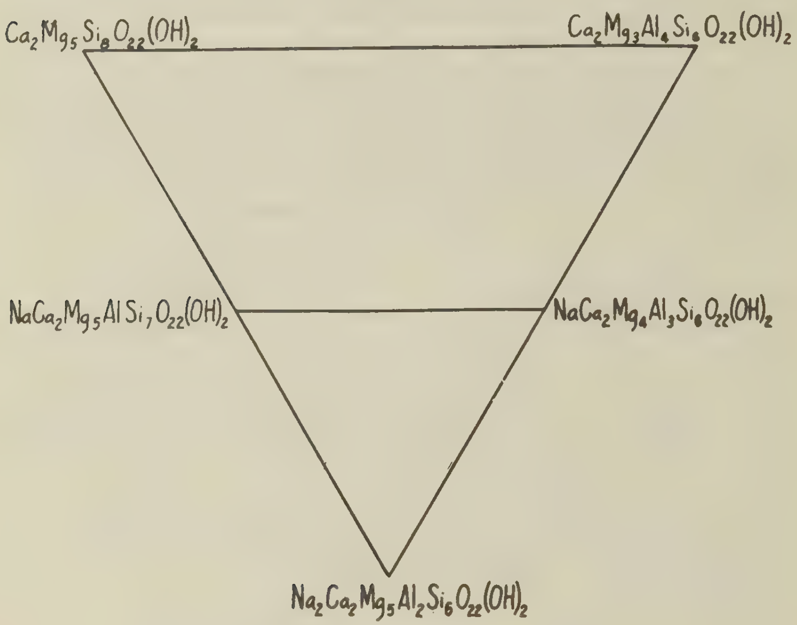
$Ca_2Mg_5Si_8O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$Na_2Ca_2Mg_5Al_2Si_6O_{22}(OH)_2$

FIG. 1. Relations of some hornblende formulas.

PART 1. COMMON HORNBLENDES

It is well known that Warren's work[2] established the correctness of Schaller's formula[3] for tremolite and also gave us the contents of the unit cell, as well as the presence of a vacant space which can be occupied by an atom of Na, thus permitting an Al atom to replace a Si atom, the total valencies being satisfied by the simultaneous introduction of one Na atom into the vacant space. Hallimond's study makes use of these facts and also shows very clearly that there is continuous variation from the tremolite formula in two different ways (disregarding the variation from Mg to Fe); these two ways are:

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[2] Warren, B. E., *Zeit. Krist.*, **72**, 493 (1930).

[3] Schaller, W. T., *U. S. Geol. Surv., Bull.* **610**, 133 (1916).

	Substitution
1. $Ca_2Mg_5Si_8O_{22}(OH)_2$ to $Na_2Ca_2Mg_5Al_2Si_6O_{22}(OH)_2$	Na_2Al_2 for Si_2
2. $Ca_2Mg_5Si_8O_{22}(OH)_2$ to $Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$	Al_4 for Mg_2Si_2

Thus three formulas are obtained all possible proportions of which may be represented by a triangle, the corners of which are used to represent these formulas. However, reliable analyses of amphibole show that the substitution of Na_2Al_2 for Si_2 extends only half as far as indicated, perhaps due to lack of more vacant spaces. Accordingly, $Na_2Ca_2Mg_5Al_2Si_6O_{22}(OH)_2$ is not an amphibole formula; it is used merely for conveneince to complete the triangle, as shown in Fig. 1. The chief end-member formulas for non-ferrous calciferous amphiboles are therefore the following four:

1. $Ca_2Mg_5Si_8O_{22}(OH)_2$
2. $Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$
3. $NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
4. $NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$

Hallimond notes that the second of these formulas is often called the Tschermak molecule; the writer would suggest that it be called tschermakite and the corresponding ferrous formula may then be called ferrotschermakite.

Hallimond has plotted nearly two hundred of the best analyses of calciferous amphiboles on such a (partial) triangle (always assuming that Mg stands for Mg and also Mn, Fe'', Fe''' and Ti). He uses the number of Si atoms $\{$for 2400 $(O+OH_2F)\}$ as one coordinate and the number of atoms in the "vacant space" as the other coordinate. This is not quite the same as using the formulas, because Na atoms can occupy such spaces as a result of other kinds of replacements, notably 2Na for Ca. The writer has attempted to plot analyses more strictly on the basis of the formulas, excluding all analyses containing more than about 10 per cent of other end-members (including soda-tremolite, glaucophane and all kinds of oxyhornblende) and also all analyses not accompanied by data on the physical properties of the samples concerned. The results are shown in Fig. 2.

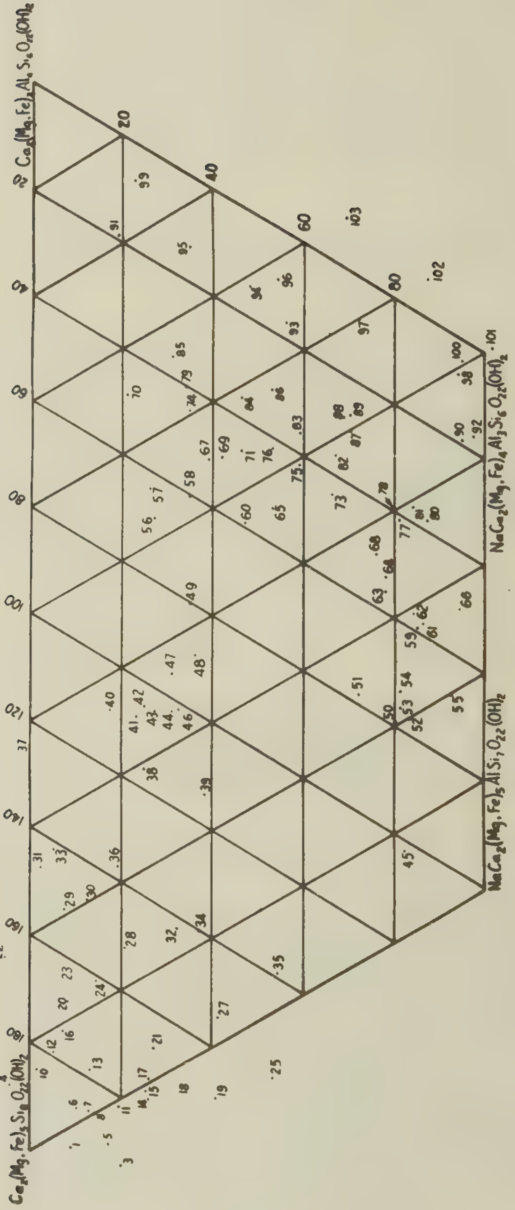
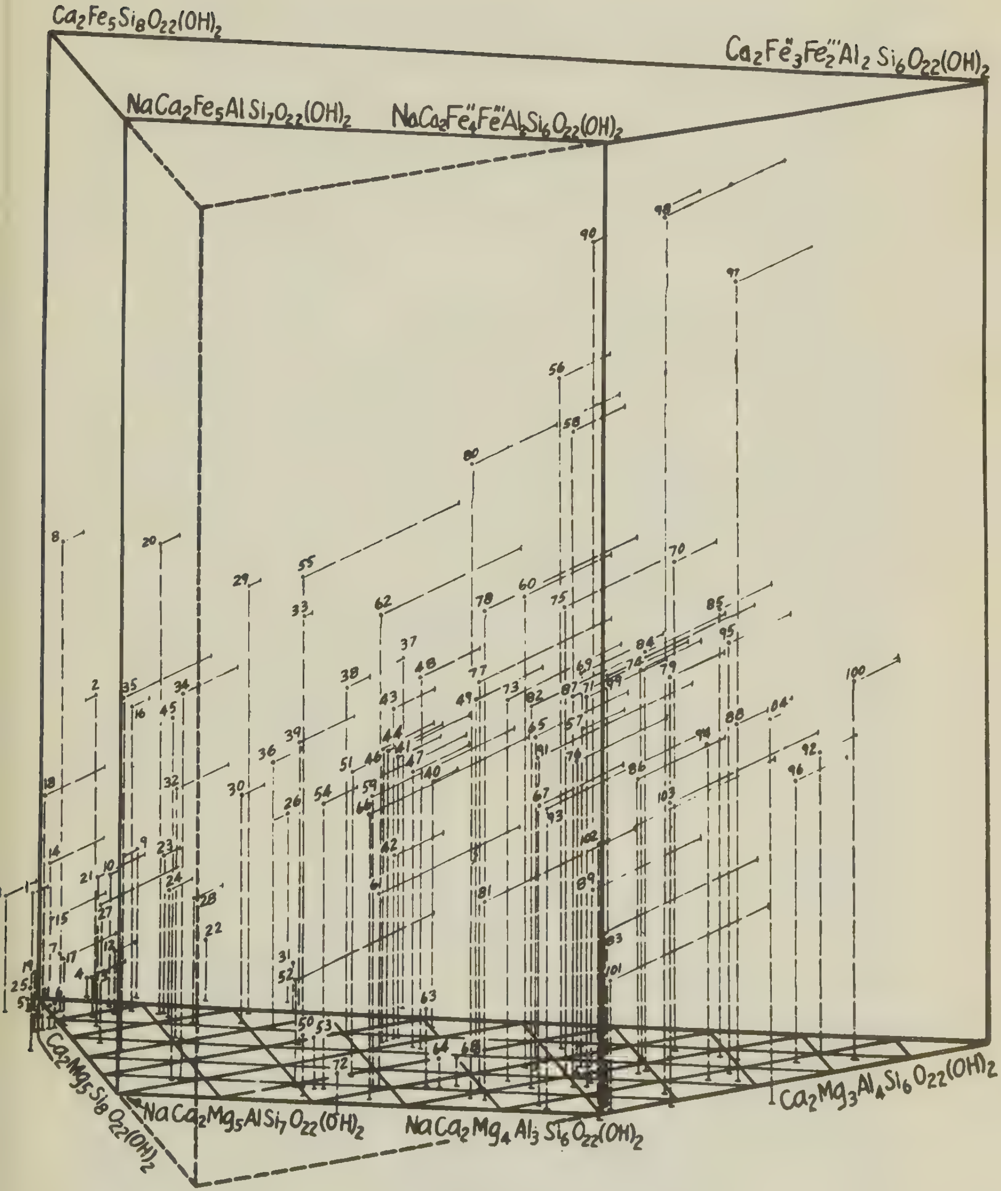


FIG. 2. Composition of selected hornblendes disregarding Mg-Fe variation. (Nos. 88 to 103 are Nos. 89 to 104 of Table 2)


$Ca_2Fe_5Si_8O_{22}(OH)_2$
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$
$NaCa_2Fe''_4Fe'''Al_3Si_6O_{22}(OH)_2$
$Ca_2Mg_5Si_8O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$
98
90
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56
58
80
8
20
29
55
33
62
78
60
75
70
85
37
48
95
84
2
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89
27
28
15
22
83
7
17
12
31
101
19
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63
50
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64
68
72

FIG. 3. Composition of selected hornblendes.

Of course physical properties vary with variations in composition but they vary more rapidly with variations in the amount of replacement of Mg by Fe than with the variations shown in Fig. 2. Accordingly it is almost impossible to discover the relations between variations in composition and variations in physical properties without considering the Mg-Fe variation. Since this variation is entirely independent of the variations shown in Fig. 2 and may affect all the end-members of that figure, it can be shown by adding a third coordinate at right angles to the others. This changes the (partial) triangle into (part of) a triangular column, as shown in Fig. 3.

To determine the position of any analysis on the vertical coordinate it is necessary to make certain assumptions. This coordinate may be considered to represent Y of Machatschki's groups[4]: $X=(Ca, Na, K)$, $Y=(Mg, Mn, Fe, Al, Ti)$ and $Z=(Si, Al)$. It is impossible to represent more than one kind of variation along the vertical coordinate. It is thought that the relation between $200\ (Mg+Al')$ and $Mg+Al'+Fe''+Mn+Fe'''+Ti$ will be the most useful. To find Al' it is only necessary to subtract from the total Al atoms the number necessary to be added to Si to make $Si+Al=800$ (on the basis of 2400 $(O+OH, F)$ atoms.) It is assumed that all Mn and Fe'' and Fe''' and Ti atoms belong to the Y group and play the role of Mg atoms. It is now rather generally accepted that AlAl may proxy for MgSi; it seems very probable that Fe''' and Ti do not proxy for Si, but replace Mg only; to keep the total valencies balanced this may be explained as a replacement of MgSi by Fe''' Al and of MgSiSi by TiAlAl. It is a fact that practically all analyses of hornblende contain enough Al atoms to permit this assumption. Accordingly, the vertical coordinate of Fig. 3 is obtained from the relation between $Mg+Al'$ and $Fe''+Fe'''+Mn+Ti$.

Even after thus obtaining the position of more than a hundred analyses of calciferous amphiboles in this (partial) triangular column, it is not a simple matter to derive nor to show the corresponding variations in physical properties. And the variations in physical characters can not correspond with the expressed variations in composition in any simple way because there are many unexpressed variations in composition which must have their effects upon the physical properties. For example, no attention is paid to the replacement of Fe'' by Fe''' or Fe'' by Mn or Fe'' by Ti, or Na by K, or OH by F. In spite of all these limitations the writer believes that an expression of the best approximation of average conditions, which can be derived, will be useful, if only as something to be improved. After constructing about fifty diagrams showing the variations of physical properties along selected lines and planes in this (partial) triangular column, and studying their mutual relations, certain conclusions have been reached.

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[4] *Zeit. Krist.*, **70**, 214 (1929).

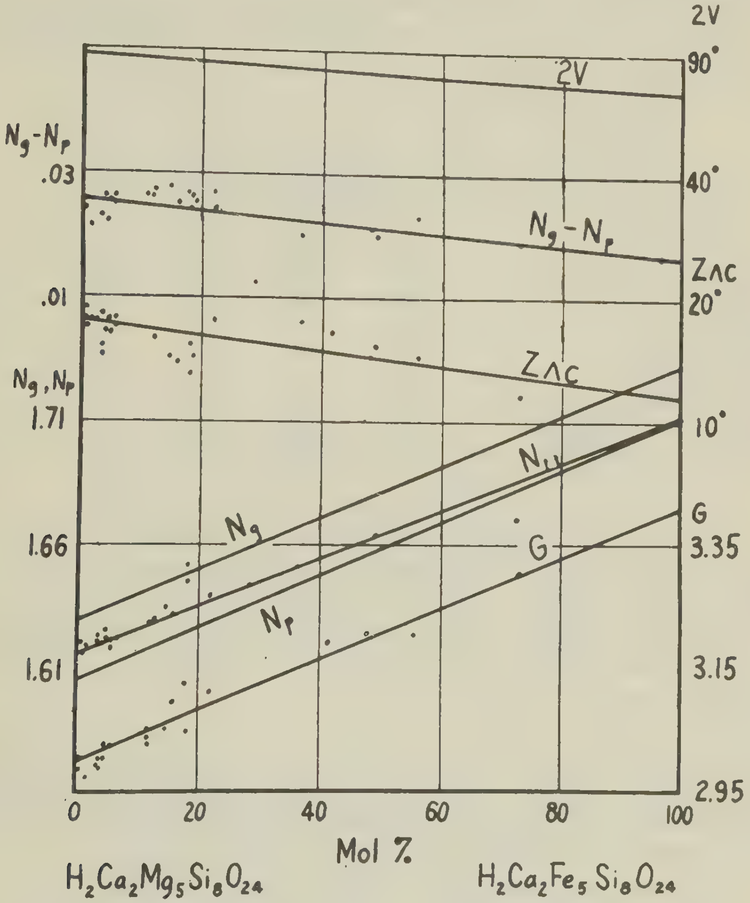

FIG. 4. The tremolite-ferrotremolite series.

First, it seems possible, now, to simplify and modify the diagram for the tremolite-ferrotremolite series first published[5] in 1931 to give the results shown in Fig. 4. This diagram gives the properties of two end-

[5] Winchell, A. N., *Am. Mineral*, **16**, 257 (1931).

members of the system. The writer is much indebted to Hallimond for an important correction[6] of the published analysis of "pargasite" from Amity, N. Y., which vitiates entirely the former diagram[7] for the series: $Ca_2Mg_5Si_8O_{22}(OH)_2-NaCa_2Mg_5AlSi_7O_{22}(OH)_2$. Estimates of the physical properties of this and other end-members of the system follow, derived (in part by extrapolation) from data on analyzed samples inside the (partial) triangular column:

TABLE 1. APPROXIMATE PROPERTIES OF END-MEMBERS

End-member	Sign	2V	N_g	N_g-N_p	$Z\wedge c$	G
$Ca_2Mg_5Si_8O_{22}(OH)_2$	(−)	88°	1.628	.03	18°	2.98
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$	(+)	50°	1.63	.02	25°	3.06
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	(+)	85°	1.64	.02	28°	3.15
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$	(−)	80°	1.657	.02	20°	3.13
$Ca_2Fe_5Si_8O_{22}(OH)_2$	(−)	75°	1.735	.025	12°	3.40
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$	(−)	20°	1.73	.02	15°	3.42
$NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$	(−)	35°	1.74	.02	18°	3.45
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$	(−)	70°	1.75	.03	18°	3.42

From these data it is possible to construct diagrams showing the variations in properties on the front faces of the (partial) triangular column (Fig. 5), on the rear face of the column (Fig. 6), on the base of the column (Fig. 7), and on the top of the column (Fig. 8). Finally, it is possible to show (in clinographic projection) the variations in properties in all parts of the column, as done in Fig. 9.

The last two formulas in Table 1 show the replacement of the five atoms of Mg(+Al) by Fe''' as well as Fe''. It should be understood that in locating any analysis in the (partial) triangular column Mn is included with Fe'' and Ti is included with Fe'''. When Ti comes into the problem, the last formula may be written: $Ca_2Fe''_4TiAl_2Si_6O_{22}(OH)_2$.

It is important to remember that this (partial) triangular column will not correspond with the facts in every case; indeed it will only rarely correspond with all the data—it is only an estimate of the *average* condition. But it is believed that it will give an *approximately* correct idea of the composition of a sample of amphibole belonging to this system. The amphiboles belonging to this system include tremolite, actinolite, ferrotremolite, pargasite, hastingsite and "common hornblende," but do not include cummingtonite, grunerite, soda-tremolite, oxyhornblende, glauco-

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[6] Hallimond, A. F., *Am. Mineral.*, **28**, p. 79, note 107 (1943).

[7] Winchell, A. N., *Am. Mineral.*, **16**, 260 (1931).

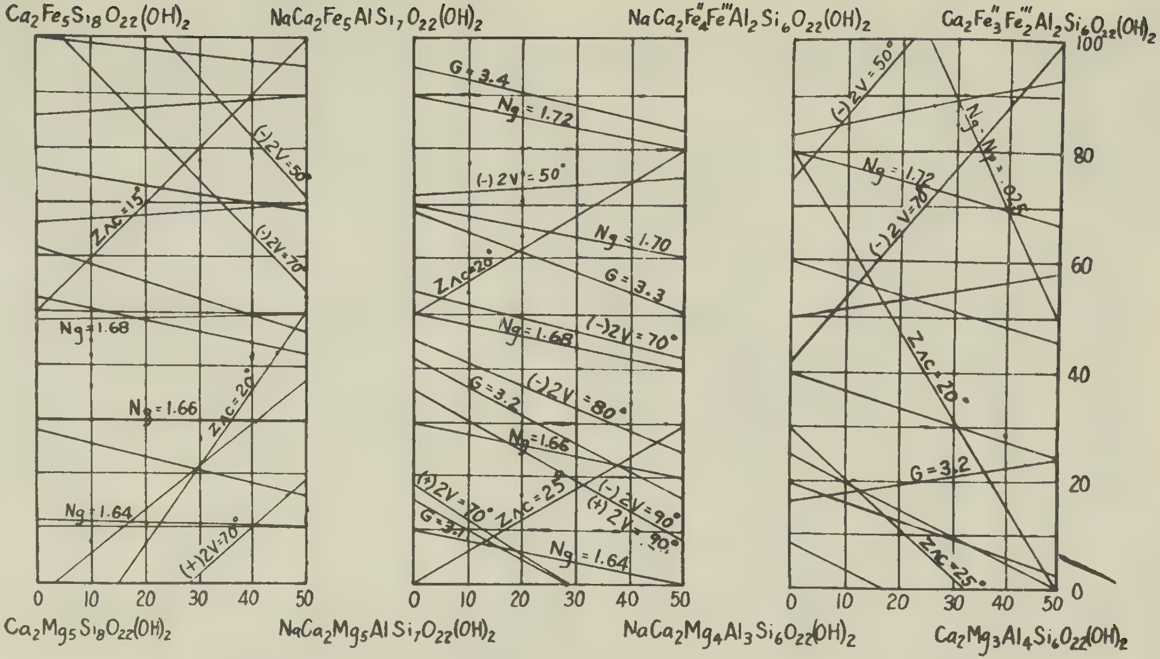

FIG. 5. Properties on the front faces of the (partial) triangular prism (hornblende).

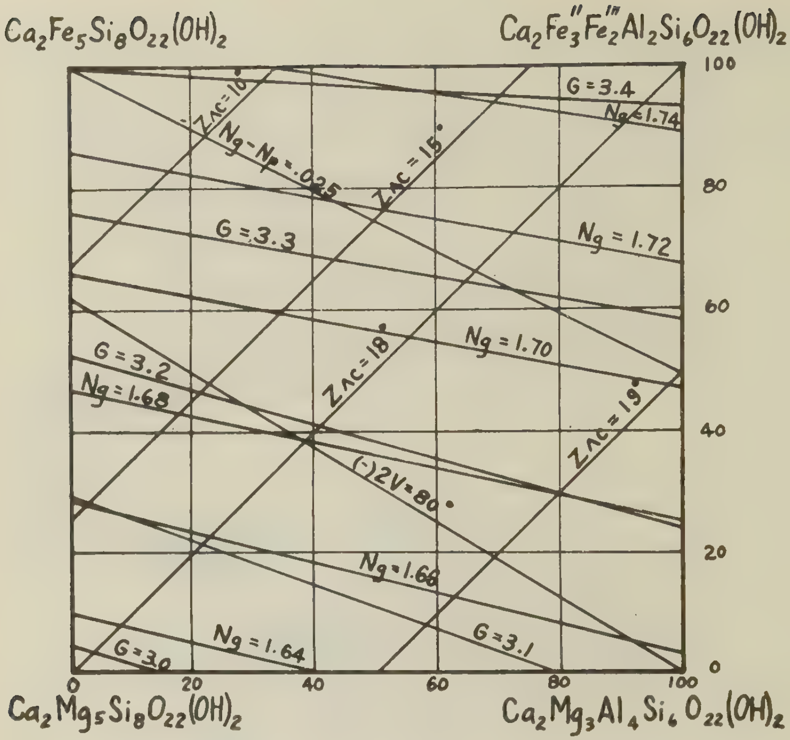

FIG. 6. Properties on the rear face of the (partial) triangular prism (hornblende).

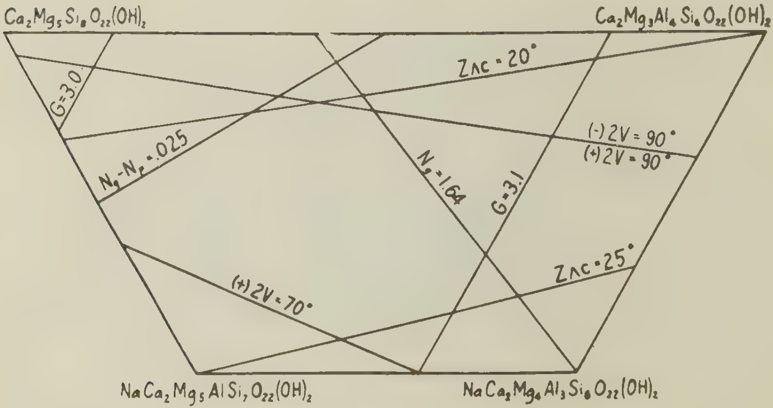

FIG. 7. Properties on the bottom of the (partial) triangular prism (hornblende).

phane, riebeckite, arfvedsonite and intermediate types sometimes called "soda-amphiboles."

For many years the writer has prepared diagrams showing the relations between physical properties and composition on the basis of molecular (or atomic) percentages. It was very surprising to him to find in a recent publication[8] the statement: "Optic properties in general are more nearly a function of density (weight percentage) than of number of ions (molecular percentage)." As long ago as 1878 Dufet[9] proved that the contrary statement is true for orthorhombic crystals. In 1894 Lavenir[10] confirmed Dufet's results and extended them.[11] In 1925 Porter[12] proved that the index of refraction is a rectilinear function of the composition *expressed in molecular percentage* for rays vibrating along the axis of symmetry in monoclinic minerals, and, in general, is more simply related to molecular percentage composition than to the weight percentage composition in all crystals. But the relationship is not necessarily nor usually exactly rectilinear in triclinic crystals nor in monoclinic crystals except along the *b* axis.

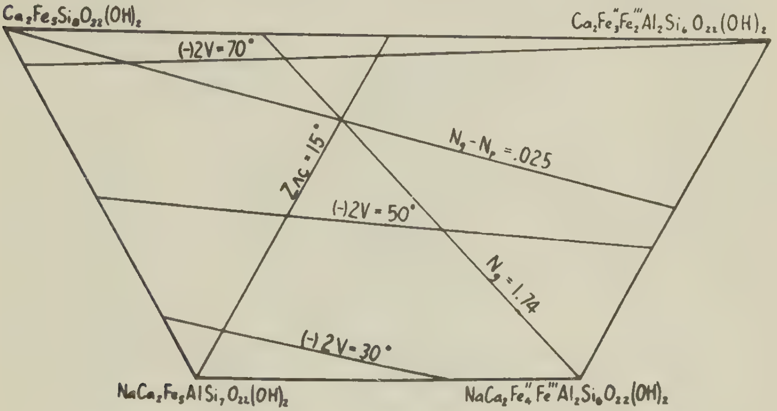
$Ca_2Fe_5Si_8O_{22}(OH)_2$
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$
(-)2V = 70°
$Z \wedge c = 15°$
$N_g - N_p = .025$
(-)2V = 50°
$N_g = 1.74$
(-)2V = 30°
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$
$NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$

FIG. 8. Properties on the top of the (partial) triangular prism (hornblende).

Table 2 gives the number of atoms (or ions) of each constituent in 104 analyses of calciferous amphiboles on the basis of 2400 atoms of oxygen

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[8] Folinsbee, R. E., *Am. Mineral.*, **26**, 498 (1941).

[9] *Bull. Soc. Fr. Min.*, **1**, 58 (1878).

[10] *Bull. Soc. Fr. Min.*, **17**, 153 (1894).

[11] Among minerals there seem to be some as yet unexplained exceptions to this rule, as illustrated in the triphylite-lithiophilite series and in the new data for the orthorhombic pyroxene, enstenite.

[12] Porter, Mary W., *Proc. Roy. Soc.*, **109**, 78 (1925).

TABLE 2. ATOMIC RATIOS OF CALCIFEROUS AMPHIBOLES FOR (O, OH, F) = 2400

No.	Si −600	Al	Fe'''	Fe''	Mn	Ti	Mg	Ca	Na	K	H	F	Ca+Na+K −200	$\frac{200(Mg+Al')}{Mg+Al'+Fe}$	Hallimond's No.	Reference
1	195	23	11	50	3	1	466	189	15	5	77		9	176	2	1
2	192	51	24	135	4		329	178	9	4	96		−9	139	4	1
3	192	20	15	48	2	2	468	190	21	9	63	7	20	176	5	1
4	190	22		7	1		485	188	6	1	197	7	−5	197	9	1
5	190	21	2	2	1		509	190	18	9	106	33	17	198	13	1
6	187	29		6		2	490	193	13	4	142	16	10	197	12	1
7	186	17		22		8	458	190	18	5	209		13	188	10	1
8	186	49	31	217	7		248	176	31	7	61	14	14	105	15	1
9	186	20	8	64	3		442	181	5	5	168	2	−9	171	16	1
10	184	20	2	61	3		450	185	13	3	182		1	175		2
11	182	20	2	2		1	485	205	11	3	202	5	19	198	18	1
12	179	21	6	20	6		477	186	15	4	161	41	5	188	20	1
13	178	2		17			483	200	10	3	136		13	193		3
14	177	57		88			398	158	68		164		26	166	19	1
15	176	37	14	43			463	186	25	14	56	58	25	179	22	1
16	174	45	12	139		3	325	190	15	2	194		7	138	25	1
17	173	21	8	27			474	181	33	12	183	27	26	186		4
18	173	24	0	114	2	2	378	193	39		214		32	152	26	1
19	169	75	5	22		3	450	194	35	12	80	11	41	188		5
20	168	34	32	211			257	192	16		194		8	103	29	1
21	167	34	23	50	2	2	446	184	32	11	36	111	27	171	30	1
22	167	22		27	2	1	484	192	2		123		−6	188		6
23	165	42	27	52		1	422	180	22	5	148	34	7	169	32	1
24	161	49	16	48			426	199	15		200		14	174	35	1
25	159	36	9	17	2		466	169	65	19	200	37	53	189	34	1
26	159	60	5	86	2	2	394	188			221		−12	162	36	1
27	154	62	13	51	Ni 3		401	196	31	14	212		41	172	42	1
28	151	106	7	56	2	5	429	203	13	4	42		20	175	38	1
29	151	40	28	185			280	171	26	10	254		7	114	33	1
30	147	45	33	80	9	3	410	182	21	9	136	41	12	153	44	1
31	146	38	2	21		1	486	187	8	2	148		2	190		7
32	142	124	23	68	3	4	349	210	12	10	91		32	162	48	1
33	141	68	31	176			284	195	10		217		5	117	50	1
34	140	83	33	147	2	4	325	192	33	12	98		37	130	49	1
35	139	160	2	194	4	11	279	203	13	38	17		54	128		8
36	137	21	32	103	2	8	391	187	32		243	19	19	146		9
37	124	118	37	151		3	304	183	9	5	140		−3	129	57	1
38	116	101	72	95	2	13	312	178	34	13	134	12	25	129	59	1
39	114	67	66	103	3	1	380	206	31	1	119		38	137		10
40	109	155	17	107	14	3	358	198	14	5	66		17	150		11
41	107	133	39	100	2	12	337	184	29	10	61	64	23	142	62	1
42	104	98	31	61		8	429	200	22	3	160		25	163	64	1
43	104	110	60	96	2	16	322	187	28	12	157		27	132	65	1
44	102	124	27	116	1	12	343	175	53	3	166		31	141	66	1
45	102	115	16	152		10	289	199	83		198		82	126		12
46	101	118	40	104		5	338	204	28		180		32	142	67	1
47	95	125	22	125			352	197	27	7	203		31	143	69	1
48	89	212	9	156		21	207	208	28		129		36	125		13
49	80	166	54	113	4	19	292	175	39	21	64	37	35	128	75	1
50	79	183	7	20		1	433	189	69	22	67		80	189	79	1
51	78	176	22	121		11	289	183	79	10	176		72	138	77	1
52	77	146	11	40	2	4	457	189	79	15	100	31	83	179		14
53	76	178	8	18			433	183	73	25	93	81	81	190	80	1

TABLE 2—*Continued*

No.	Si −600	Al	Fe‴	Fe″	Mn	Ti	Mg	Ca	Na	K	H	F	Ca+Na+K −200	$\frac{200(\mathrm{Mg}+\mathrm{Al}')}{\mathrm{Mg}+\mathrm{Al}'+\mathrm{Fe}}$	Hallimond's No.	Reference
54	73	138	50	101	1	1	379	211	35	35	25	57	81	143		15
55	68	100	141	150	1	13	271	213	68	11			92	94	84	1
56	68	163	28	294	17	22	128	184	30	13	176		27	61		16
57	63	165	66	84	2	19	317	175	34	17	168		26	134	88	1
58	60	154	17	228	1	23	166	172	47	16	229		35	80	93	1
59	59	141	46	94	3	16	378	206	39	40	32	66	85	140		17
60	59	227	21	221	2	15	195	193	31	23	88		47	104	95	1
61	58	203	13	27	1	5	430	197	74	15	94	11	86	182	98	1
62	57	203	43	187	2	21	202	230	33	21	52		84	102	101	1
63	56	162	10	20	1	9	463	193	67	18	43	138	78	185	99	1
64	53	227	4	12	1		430	190	78	10	127	12	78	194	103	1
65	53	198	53	112	2	20	304	177	60	16	79		53	131	102	1
66	51	196	52	93	4	10	324	185	72	37	73	23	94	140	106	1
67	51	194	34	98	1	17	348	189	44	16	116		49	145		18
68	50	233	3	9	1		426	192	75	9	128	14	76	195	107	1
69	49	183	56	109	2	41	269	186	36	21	93	41	42	118	108	1
70	48	174	45	177	2	6	213	177	18	26	336		21	101		19
71	46	181	27	153		15	295	191	55		203		46	125	110	1
72	45	204	3	9	1	7	437	202	76	32	68	125	110	192		20
73	44	201	54	143		10	277	186	57	23	163		66	122	113	1
74	44	189	36	160		18	272	181	41	13	200		35	117	115	1
75	42	207	78	158	5	9	221	190	49	20	122		59	104		21
76	42	258	25	132	4	4	259	181	60	12	145		53	137	116	1
77	41	209	31	182	3	17	254	189	73	19	62	39	81	113	109	1
78	40	217	33	185	2	33	209	210	47	23	70		80	102	118	1
79	40	219	116	98			279	207	27				34	122		22
80	38	178	108	215		12	167	178	83	26	96	19	87	71	119	1
81	37	238	19	59		14	328	175	88	21	192		84	163	121	1
82	36	186	70	103		28	289	188	79		136		67	121		23
83	36	214	3	72		8	409	197	38	24	49	105	59	169	125	1
84	36	208	51	162		5	251	176	47	23	210		46	115	122	1
85	36	194	41	187		13	254	181	40	10	204		31	109	120	1
86	31	228	33	133		2	309	186	53	14	156		53	137	130	1
87	30	209	57	137		15	276	197	50	23	132		70	120	132	1
88	29	206	37	111	2	31	305	185	31	19	136	39	35	131	135	1
89	28	267	18	74	1	2	295	189	58	22	224		69	161		24
90	27	209	82	372			34	197	39	34	138		70	27	137	1
91	19	252	29	128	2	31	259	201	67	27	77	17	95	127		25
92	19	233	65	96	2	11	317	185	19	15	150		19	138	141	1
93	17	263	16	38		5	385	213	57	27	106	10	97	177	152	1
94	17	200	44	107	1	26	323	186	58	12	197		56	131	146	1
95	14	211	44	149		28	252	184	53	11	230		48	111	148	1
96	13	294	29	112	1	8	259	172	47	16	198		35	142	150	1
97	10	237	51	353	17	39	53	170	57	27	65		54	36	153	1
98	8	207	92	341	13	11	33	169	64	39	217		72	19	154	1
99	7	235	84	138	13	4	263	198	50	46	78	3	94	112	156	1
100	7	191	187	3	1	2	296	192	29	2	224		23	121		26
101	4	253	21	42	1	5	399	203	65	27	33	137	95	174	158	1
102	−2	251	53	72	3	20	330	203	64	35	60	35	102	142		27
103	−7	241	78	29	1	57	334	187	54	46	43		87	139		28
104	−10	239	56	86	2	24	304	196	67	6	203		69	133		29

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(plus hydroxyl plus fluorine). For convenience the number of Si atoms is given after subtracting 600, since it then gives directly one coordinate needed to locate the analysis in Figs. 2 and 3. Another coordinate is given in the column headed $Ca+Na+K-200$. And the third coordinate is in the column headed $200\,(Mg+Al')$ divided by $Mg+Al'+Fe$, in which Fe stands for Fe'', Fe''', Mn and Ti.

Table 3 gives the physical properties of these 104 analyzed samples of calciferous amphiboles, so far as they have been determined. More measurements of these properties on analyzed samples are much needed, especially in the case of hornblende rich in iron.

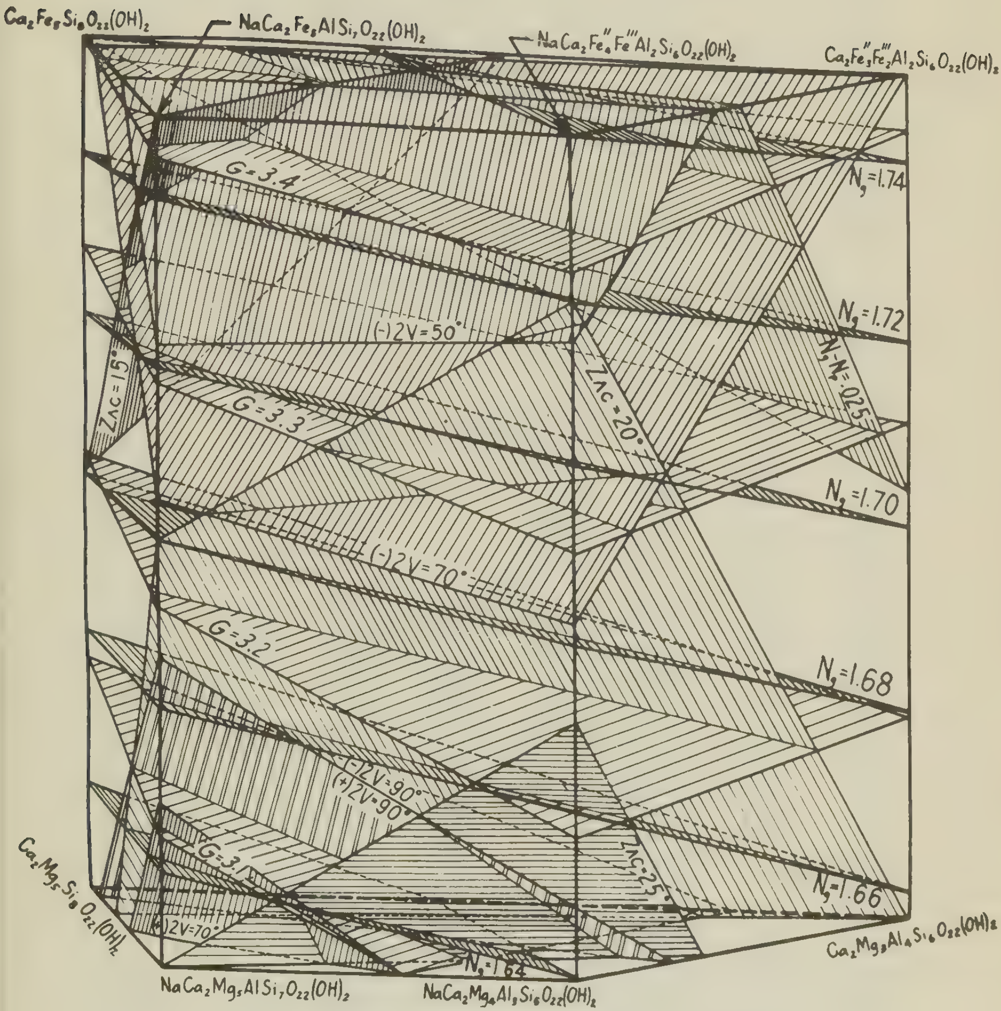
$Ca_2Fe_5Si_8O_{22}(OH)_2$
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$
$NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$
G=3.4
N_g=1.74
(-)2V=50°
N_g=1.72
Z∧c=15°
Z∧c=20°
N_g-N_p=.025
G=3.3
N_g=1.70
(-)2V=70°
G=3.2
N_g=1.68
(-)2V=90°
(+)2V=90°
G=3.1
Z∧c=25°
N_g=1.66
(+)2V=70°
N_g=1.64
$Ca_2Mg_5Si_8O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$

FIG. 9. Physical properties of calciferous hornblendes.

TABLE 3. PHYSICAL PROPERTIES OF CALCIFEROUS AMPHIBOLES

No.	Sign	2V	N_g	N_m	N_p	N_g-N_p	$Z\wedge c$	G
1	–		1.634	1.626	1.616	0.018	18°	3.044
2	–		1.653	1.642	1.628	0.025	15°	3.131
3	–		1.639	1.626	1.611	0.028	17°	3.051
4	–	79°38′	1.6272	1.6155	1.6000	0.0272	15°25′	2.98
5	–	88°23′	1.6246	1.6132	1.5992	0.0254	20°1′	2.997
6	–	86°29′	1.6347	1.6192	1.6022	0.0325	16°38′	2.980
7	–		1.632		1.609	9.023		
8	–		1.659	1.649	1.631	0.028	24–27°	3.126
9	–	81°38′	1.6450	1.6330	1.6173	0.0277	14°59′	3.047
10	–	79°49′	1.6410	1.6297	1.6139	0.0271	16°31′	3.047
11	–	82°	1.6307	1.6183	1.6024	0.0283	15°30′	
12	–	87°56′	1.6299	1.6171	1.6036	0.0263	18°18′	3.025
13	–	80°	1.631	1.620	1.608	0.023	17°	2.989
14			1.6529		1.6267	0.0262	14°34′	3.116
15	+		1.634	1.621	1.613	0.021	17°	3.056
16	–		1.650	1.641	1.627	0.023	20°	3.11
17	–	84°5′	1.6319	1.6210	1.6065	0.0254	16°54′	3.031
18	–		1.641	1.630	1.617	0.024	18°	3.09
19		83°				0.0241	16°	2.996
20			1.663		1.642	0.021	15°	3.211
21	–		1.637	1.628	1.618	0.019	19°	3.064
22	–	78°30′	1.632	1.620	1.607	0.025	17°30′	
23	–	81°30′	1.6412	1.6304	1.6162	0.0250	14°27′	3.092
24			1.638		1.615	0.023	18°	
25	–	86°14′	1.6244	1.6134	1.6017	0.0227	19°31′	3.03–3.04
26	–	Lg.	1.638	1.629	1.618	0.020	17°	3.06
27	–		1.650		1.628	0.022		
28	–		1.642	1.634	1.625	0.017	12°	3.054
29	–		1.664	1.652	1.637	0.027	20°	
30	–	84°8′	1.6503	1.6382	1.6237	0.0266		3.111
31	–	81°30′	1.634	1.624	1.612	0.022	18°	
32	–	Lg.	1.642	1.631	1.618	0.024	16°	3.147
33	–		1.659		1.638	0.021	17°	3.188
34	–		1.647	1.645	1.631	0.016	18°	3.171
35	+		1.672	1.660	1.649	0.023		3.18
36	–	76°	1.652	1.642	1.626	0.026	16°	3.11
37	–	83°57′	1.6678	1.6551	1.6416	0.0262	15°30′	
38	–	78°	1.664	1.655	1.643	0.021	19°	3.159
39	–	70°	1.654	1.646	1.627	0.027	17°	3.12
40	–	88°30′	1.661		1.636	0.025	16°	3.12
41	–	75°	1.670	1.662	1.651	0.019	19°	3.160
42	–		1.654		1.633	0.021		3.110
43	–	76°	1.671	1.663	1.653	0.018	20°	3.159
44	–	81°	1.652	1.642	1.629	0.023	25°	
45	–	77°	1.666	1.657	1.643	0.023	15°	3.15
46	–		1.661		1.641	0.020		3.18
47	–		1.658		1.640	0.018	17°	3.182
48	–	79°	1.675	1.665	1.650	0.025	19°	3.18
49	–		1.680	1.675	1.652	0.028	14°30′	3.188
50	+	60°29′	1.6351	1.6180	1.6131	0.0220	26°	3.069
51		78–82°	1.658		1.638	0.020	14°30′	
52	+	60°	1.645	1.630	1.622	0.023	27°	

TABLE 3—*Continued*

No.	Sign	2V	N_g	N_m	N_p	N_g-N_p	$Z\wedge c$	G
53	+	58°51′	1.6353	1.6205	1.6158	0.0195	26°57′	3.095
54	+	74°	1.654	1.644	1.638	0.016	21°	3.20
55	−	75°44′	1.6798	1.6729	1.6598	0.020	14°40′	3.21
56	−	59°	1.701	1.692	1.673	0.028	15°+	
57	−	77°	1.669	1.660	1.651	0.018	18°	3.164
58	−	77°	1.700	1.687	1.666	0.034	22°	
59	+	76°	1.654	1.643	1.636	0.018	22°	3.20
60	−	75°		1.675		0.016	18°	3.27
61	+	66°	1.6429	1.6284	1.6218	0.0211	24°	
62	−	70°	1.684	1.676	1.660	0.024	17°	3.254
63	−	83°	1.638	1.631	1.622	1.016	20–22°	3.090
64	+	70°	1.6430	1.6291	1.6221	1.0209	21°	
65	−	Lg.	1.683	1.673	1.658	0.025	13°30′	
66	−	88°	1.6665	1.6589	1.6511	0.0154	23°	
67	−	81°	1.666	1.652	1.633	0.033	15°	3.15
68	+	64°	1.6416	1.6265	1.6206	0.0210	22°	
69	−	71°	1.673	1.665	1.654	0.019	17°	3.176
70	−	77°6′	1.673	1.659	1.651	0.022	25°	3.15
71	−		1.574		1.653	0.021		
72	+	52°9′	1.6332	1.6180	1.6142	0.0190	27°30′	3.11
73	−		1.678		1.658	0.020	24°	3.268
74	−		1.676		1.657	0.019	18°	3.26
75	−		1.681		1.661	0.020		3.292
76	−	86°	1.674	1.663	1.651	0.023	16°15′	3.171
77	−	81°42′	1.6789	1.6701	1.6583	0.0206	23°48′	3.285
78	−	66°30′	1.679	1.674	1.661	0.018	13°30′	3.278
79	−	80°4′	1.6843	1.6753	1.6648	0.0195	16°	
80	−	38°	1.7000	1.6980	1.6804	0.0198	20°	
81	−	85°	1.659	1.647	1.636	0.023	21°22′	3.13
82	−	86°	1.673	1.662	1.647	0.026	20°	3.18
83	+	63°1′	1.6519	1.6380	1.6329	0.0190	26°15′	3.186
84	−		1.677		1.658	0.019		3.284
85	−	65°38′	1.681	1.673	1.659	0.022	16°30′	3.234
86	−		1.671		1.652	0.019		3.214
87	−		1.678		1.658	0.020	16°	3.258
88	−	70°	1.672	1.664	1.650	0.022	15°	3.170
89		72–74°	1.668		1.635	0.033	15–17°	3.258
90	−	Sm.	1.713	1.710	1.693	0.020	17°	
91	−	73°	1.697	1.691	1.680	0.017	19°	3.267
92				1.65			26°	3.13
93	+	64°5′	1.6530	1.6384	1.6327	0.0203	26°20′	3.18
94	−	75°	1.677	1.669	1.652	0.025	26°	
95	−	78°	1.683	1.674	1.658	0.025	23°	
96	−	84°	1.672	1.661	1.648	0.024	19°	3.20
97	−	47°	1.722	1.719	1.698	0.024	20°	3.375
98	−	16°	1.714	1.713	1.697	0.017	(Y) 15°	
99				1.68				3.283
100	−	79°38′	1.6823	1.6743	1.6576	0.0207	20°	3.224
101	−	88°	1.641	1.632	1.622	0.019	18–19°	3.163
102	−	80°	1.685	1.674	1.665	0.020	26°30′	3.189
103	−	83°	1.718	1.700	1.676	0.042	13°	3.221
104	−	80°	1.685	1.671	1.658	0.027	22°6′	3.187

PART 2. OXYHORNBLENDES

The careful study of the changes in hornblende at about 800°C by Barnes[13] showed very clearly the relation between "common hornblende" and oxyhornblende. He proved that ordinary hornblende is changed to oxyhornblende by heating to 800°C. and that the chemical change is loss of hydrogen (not water) and oxidation of ferrous iron. He proved that amphibole with practically no iron undergoes practically no change. Therefore ordinary hornblendes containing no iron have the same composition and the same properties as oxyhornblendes free from iron. They are more appropriately known as ordinary hornblendes because they have suffered no oxidation, but they nevertheless are end-members of the oxyhornblende system. Consequently Fig. 7 shows the composition and properties of iron-free oxyhornblendes as well as those of common hornblendes. It may therefore be used as the base of a (partial) triangular prism showing the relations between composition and properties in all parts of that portion of the hornblende system which is the subject of this study—that is, those oxyhornblendes containing the normal tenor of Ca(+Na+K).

There are only a few samples of calciferous oxyhornblendes which have been analyzed and measured optically. In Table 4 available analyses are given after being recalculated to show atomic ratios for 2400 (O+OH, F), as well as the coordinates used in plotting these analyses, namely: $Ca+Na+K-200$, and $200\ (Mg+Al')$ divided by $Mg+Al'+Fe''+Mn+Fe'''+Ti$, just as in the case of ordinary hornblendes. The optical properties of these oxyhornblendes are given in Table 5, which also shows the properties of the ordinary hornblendes from which some of these oxyhornblendes were derived by heating.

The sample of hornblende from Frankfort, Pa. (No. 13 of Table 4), which was studied optically by V. E. Barnes in 1930 was analyzed in 1935 by Ray Wilcox with the following results: SiO_2 41.53, Al_2O_3 9.31, Fe_2O_3 9.54, FeO 13.69, MgO 8.14, CaO 10.60, Na_2O 1.04, K_2O 0.79, H_2O 5.35, TiO_2 0.67, MnO 0.04, F 0.33; Sum $101.03-0.14$ (for $2F=O$) $=100.89$. This shows an extraordinarily high tenor of water, but supplies a hornblende very near to tschermakite, whose properties after oxidation are known.

The eighteen analyzed samples of oxyhornblendes of Table 4 are plotted in Fig. 10 according to the same rules used in plotting the analyses of ordinary hornblendes in Fig. 2. Most of these amphiboles were ordinary hornblendes as analyzed; their optical properties were measured, and then they were changed to oxyhornblendes by heating, and the optical properties remeasured. Therefore it seems reasonable to label the end-members as if the minerals were ordinary hornblendes. The proper formulas for oxyhornblendes will be discussed later.

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[13] Barnes, V. E., *Am. Mineral.*, **15**, 393 (1930).

TABLE 4. ATOMIC RATIOS OF CALCIFEROUS OXYHORNBLENDES FOR (O, OH, F) = 2400

No.	Si −600	Al	Fe'''	Fe''	Mn	Ti	Mg	Ca	Na	K	H	F	Ca+Na+K −200	$\frac{200(Mg+Al')}{Mg+Al'+Fe}$	Reference
1	182	20	2^b	2^b		1	485	205	11	3	202^b	5	19	198	1
2	141	68	31^b	176^b			284	195	10		217^b		5	118	2
3	110	110	64^b	147^b	5	4	286	154	89	27	116^b	10	70	116	1
4	72	134	160	35	5	23	298	178	39	21	20	17	38	115	3
5	58	203	13^b	27^b	1	5	430	197	74	15	94^b	11	86	183	1, 4
6	53	227	4^b	12^b	1		430	190	78	10	127^b	12	78	194	1, 4
7	51	196	141	4	4	10	324	185	72	37	5	23	94	140	1
8	50	233	3^b	9^b			426	192	75	9	128^b	14	76	195	1, 4
9	45	204	3	9	1	7	437	202	76	32	68	125	110	192	1, 5
10	38	178	274	53	tr	12	167	178	83	26	8	19	87	70	1
11	36	208	51^b	162^b		5	251	176	47	23	210^b		46	115	2
12	7	222	137	102		28	222	200	67	20	46		87	97	2
13	1	158	104^b	164^b	1	7	176	164	29	14	516^b	15	7	78	1
14	0	210	131	3	9	33	315	187	70	29	122^*		86	130	6
15	−1	226	85	80		46	289	194	66	28	72		88	120	2
16	−3	231	76	64		48	303	199	81	18	67		98	128	2
17	−7	241	78	29	1	57	334	187	54	46	43		87	138	7
18	−8	262	86	47		29	320	197	65	23	57		85	140	2

[b] Before heating.

* From ignition.

REFERENCES FOR TABLE 4.

1. Barnes, V. E., *Am. Mineral.*, **15,** 393 (1930). No. 1 is tremolite from Ossining, N. Y. No. 3 is hornblende from Eganville, Ont. No. 5 is pargasite from Warwick, N. Y. No. 7 is hornblende from Lanark Co., Ont. No. 8 is pargasite from Amity, N. Y. No. 9 is hornblende from Argenteuil Co., Quebec. No. 10 is hornblende from Renfrew Co., Ont. No. 13 is hornblende from Frankfort, Pa.
2. Kunitz, W., *N. Jahrb. Min. B. B.* **60,** 176 (1930). No. 2 is actinolite from New Hampshire, No. 11 is hornblende from Arendal. No. 12 is basaltic hornblende from Tejedatal. No. 15 is basaltic hornblende from Isleta Crater. No. 16 is basaltic hornblende from Madeira. No. 18 is basaltic hornblende from Grosspriessen.
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4. Winchell, A. N., *Am. Mineral.*, **16,** 259 (1931). No. 5 is pargasite from Warwick, N. Y. No. 6 is pargasite from Edenville, N. Y. No. 8 is pargasite from Amity, N. Y.
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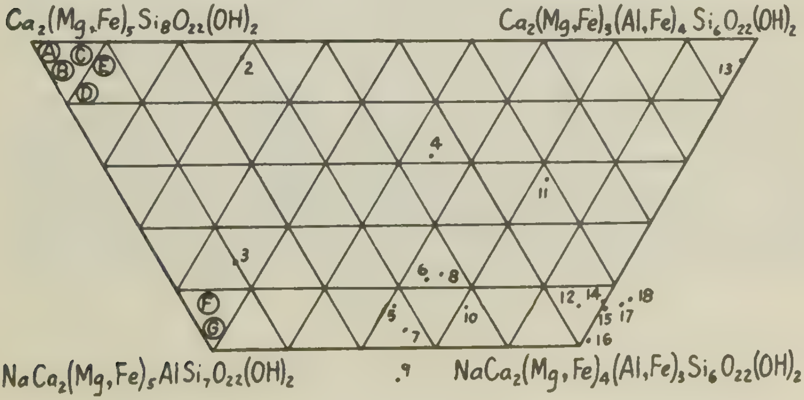
7. Parsons, A. L., *U. Toronto Geol. Stud.*, **29,** 29 (1930). Amphibole from Lochkow, Bohemia.


$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
$Ca_2(Mg,Fe)_3(Al,Fe)_4Si_6O_{22}(OH)_2$
Ⓐ
Ⓒ
Ⓑ
Ⓔ
Ⓓ
2
13
4
11
3
6
8
12
14
18
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5
10
15
17
7
16
$NaCa_2(Mg,Fe)_5AlSi_7O_{22}(OH)_2$
9
$NaCa_2(Mg,Fe)_4(Al,Fe)_3Si_6O_{22}(OH)_2$

TABLE 5. OPTICAL PROPERTIES OF CALCIFEROUS OXYHORNBLENDES

No.	Sign	2V	N_g	N_m	N_p	N_g-N_p	$Z \wedge c$	
1	−	82°	1.6307	1.6183	1.6024	0.0183	15½°	Before heating
1	−	82°	1.6308	1.6178	1.6026	0.0182	18°	After heating
2			1.659		1.638	0.021	17°	Before heating
2			1.676		1.655			After heating
3	−	63°	1.6702	1.6656	1.6539	0.0163	32°	Before heating
3	−	61°	1.7193	1.7060	1.6666	0.0527	4°	After heating
4	−	Lg.	1.735	1.715	1.675	0.060	5°	Natural
5	+	66°	1.6429	1.6284	1.6218	0.0211	24°	Before heating
5	+	86°	1.6526	1.6402	1.6287	0.0239	21°	After heating
6	+	70°	1.6410	1.6256	1.6188	0.0222	21°	Before heating
6	+	71°	1.6430	1.6291	1.6221	0.0209	21°	After heating
7	−	88°	1.6665	1.6589	1.6511	0.0154	23°	Before heating
7	−	66°	1.7100	1.6961	1.6626	0.0474	5°	After heating
8	+	64°	1.6416	1.6265	1.6206	0.0210	22°	Before heating
8	+	70°	1.6413	1.6265	1.6190	0.0223	28°	After heating
9	+	58°	1.6331	1.6186	1.6143	0.0188	27°	Before heating
9	+	58°	1.6317	1.6204	1.6170	0.0147	25°	After heating
10	−	38°	1.7000	1.6980	1.6804	0.0198	20°	Before heating
10	−	65°	1.7960	1.7690	1.7020	0.0940	0°	After heating
11			1.677		1.658			Before heating
11			1.697		1.676			After heating
12			1.700		1.681	0.019	0°	Natural
13	−	45°	1.6980	1.6950	1.6801	0.0179	22°	Before heating
13	−	69°	1.7825	1.7564	1.7003	0.0822	0°	After heating
14	−	82°	1.731	1.711	1.685	0.046	1°	Natural
15			1.701		1.679	0.022		Natural
16			1.700		1.677	0.023	6°	Natural
17	−	83°	1.718	1.700	1.676	0.042	13°	Natural
18			1.668		1.667	0.021	3°	Natural
A	−	81°	1.6278	1.6178	1.6042	0.0236	20°	Before heating
A	−	72°	1.6367	1.6262	1.6058	0.0309	13°	After heating
B	−	77°	1.6267	1.6181	1.6041	0.0226	16°	Before heating
B	−	83°	1.6284	1.6175	1.6014	0.0270	15°	After heating
C	−	82°	1.6301	1.6201	1.6067	0.0234	18°	Before heating
C	−	70°	1.6377	1.6270	1.6053	0.0324	12°	After heating
D	−	78°	1.6403	1.6278	1.6085	0.0318	16°	Before heating
D	−	56°	1.6617	1.6532	1.6220	0.0397	11°	After heating
E	−	73°	1.6413	1.6313	1.6133	0.0280	15°	Before heating
E	−	56°	1.6728	1.6634	1.6301	0.0427	10°	After heating
F	−	72°	1.6792	1.6715	1.6578	0.0214	20°	Before heating
F	−	65°	1.7477	1.7288	1.6759	0.0718	0°	After heating
G	−	86°	1.6640	1.6510	1.6370	0.0271	10°	Before heating
G	−	65°	1.7175	1.6980	1.6507	0.0668	1°	After heating

Barnes measured the optical properties of several hornblendes (both before and after heating till oxidation occurred) which have never been analyzed. It is possible to obtain the approximate composition of these samples from Fig. 9, and thus to plot their approximate position on Fig. 10. The fact that their composition is only roughly known is suggested by indicating their position by a small circle; it is *not* intended to suggest that the correct position must be inside the circle. These samples are labeled: *A* to *G*, as follows: *A*, tremolite, Russell, N.Y.; *B*, tremolite, Natural Bridge, N.Y.; *C*, actinolite, Pierrepont, N.Y.; *D*, actinolite, Zillertal, Tyrol; *E*, actinolite, Val Malenco, Italy; *F*, hornblende, Milford, Mass.; *G*, hornblende, Tyrol.

TABLE 6. APPROXIMATE PROPERTIES OF END-MEMBERS

	Sign	2V	N_g	$N_g - N_p$	$Z \wedge c$
$Ca_2Fe''_3Fe'''_2Si_8O_{24}$	(−)	55°	1.78	.070	0°
$NaCa_2Fe''_3Fe'''_2AlSi_3O_{24}$	(−)	60°	1.79	.075	0°
$NaCa_2Fe''_2Fe'''_3Al_2Si_6O_{24}$	(−)	55°	1.80	.085	0°
$Ca_2Fe''Fe'''_4Al_2Si_6O_{24}$	(−)	55°	1.80	.095	0°

Since the chemical change involved in converting ordinary hornblende into oxyhornblende is loss of hydrogen from hydroxyl, the oxygen atom which remains in the crystal having its valence satisfied by the simultaneous change of one atom of iron from the ferrous to the ferric state, the process can result in the oxidation of only as many atoms of iron as the number of atoms of hydrogen which are driven out of the crystal. This conclusion is confirmed by the results of the analysis of the hornblende from Renfrew Co., Ont. (after complete oxidation at about 800°C) which show that even after driving out all the hydrogen an oxyhornblende may still contain ferrous iron. Therefore no oxyhornblende can contain more than two atoms of ferric iron which are due to the process of oxidation. Since the iron end-member formulas of ordinary calciferous hornblende are: $Ca_2Fe''_5Si_8O_{22}(OH)_2$, $NaCa_2Fe''_5AlSi_7O_{22}(OH)_2$, $NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$ and $Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$, the corresponding formulas for oxyhornblende must be $Ca_2Fe''_3Fe'''_2Si_8O_{24}$, $NaCa_2Fe''_3Fe'''_2AlSi_7O_{24}$, $NaCa_2Fe''_2Fe'''_3Al_2Si_6O_{24}$ and $Ca_2Fe''Fe'''_4Al_2Si_6O_{24}$.

Knowing the approximately correct position of the hornblende samples *A* to *E* on Figs. 9 and 10, their content of iron can be obtained fairly closely from Figs 4, 5 and 6. In this way it is possible to find that actual data extend only to 20 per cent of the iron molecule in the $Ca_2Mg_5Si_8O_{22}$

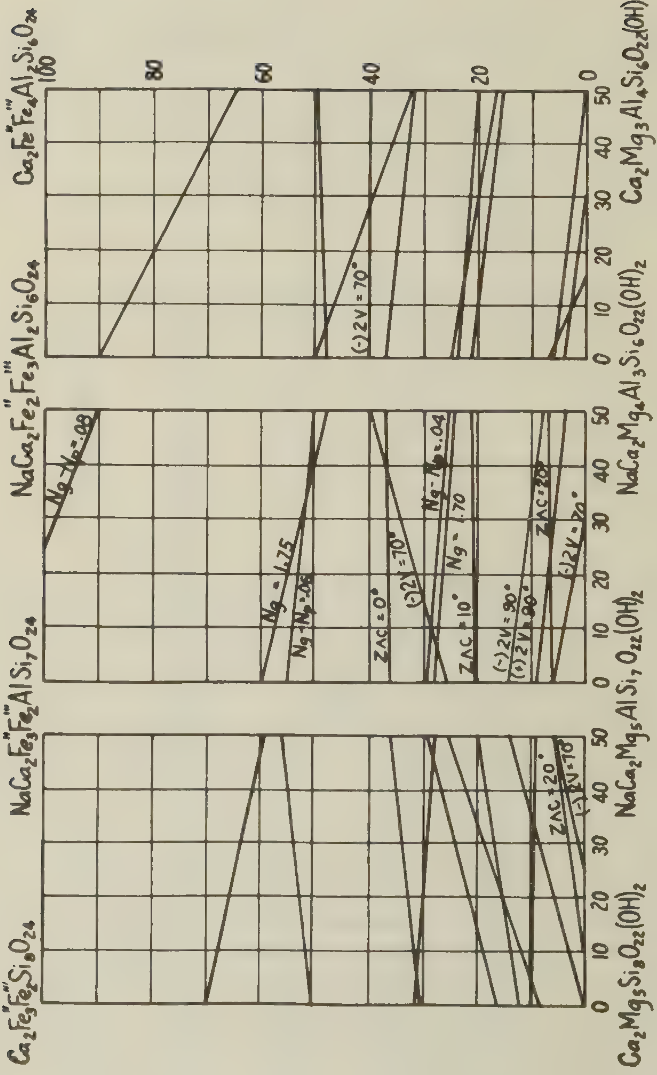

FIG. 11. Properties on the front faces of the (partial) triangular prism (oxyhornblende).

$(OH)_2$ -$Ca_2Fe''_3Fe'''_2Si_8O_{24}$ series. For all the rest of this series the properties are obtained by extrapolation, keeping in mind that only two of the five replacing Fe atoms can be oxidized, and also using the conclusions reached by Barnes that (1) the extinction angle decreases to zero, but does not become minus, and (2) the optic angle about X decreases to about 55°, but not to any value materially less, no matter how much iron may be present. It is surprising to discover that both of these changes are completed before all the oxidation is completed.

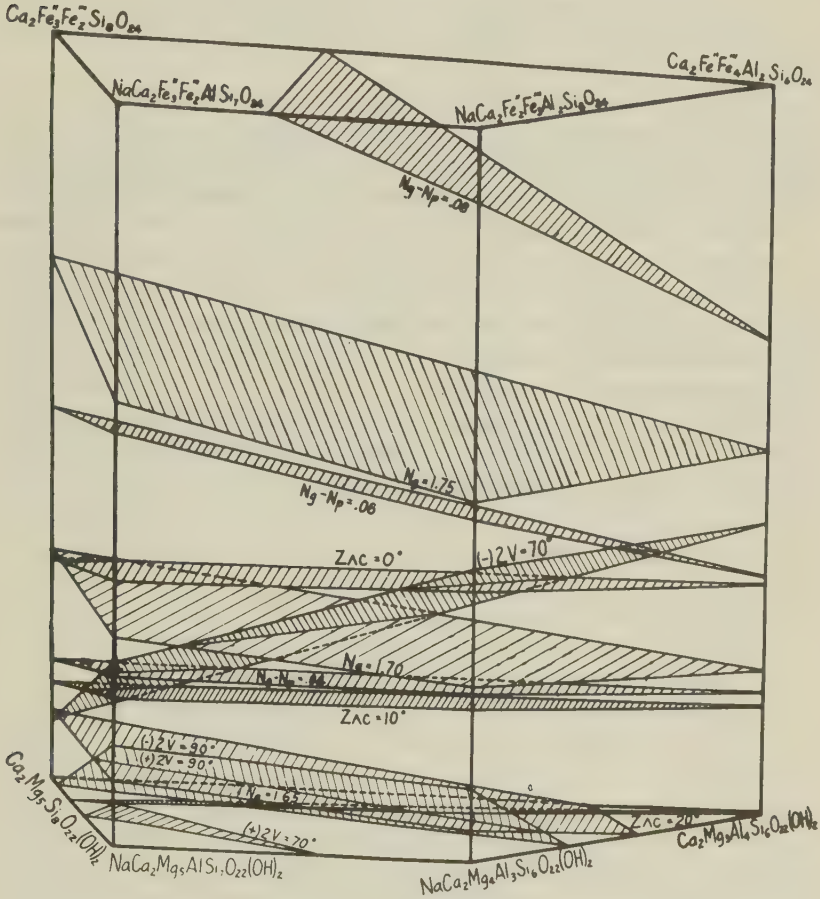
$Ca_2Fe''_3Fe'''_2Si_8O_{24}$
$NaCa_2Fe''_3Fe'''_2AlSi_7O_{24}$
$NaCa_2Fe''_2Fe'''_3Al_3Si_6O_{24}$
$Ca_2Fe''Fe'''_4Al_4Si_6O_{24}$
Ng-Np=.08
Ng=1.75
Ng-Np=.06
Z∧c=0°
(-)2V=70°
Ng=1.70
Ng-Np=.04
Z∧c=10°
(-)2V=90°
(+)2V=90°
Ng=1.65
Z∧c=20°
(+)2V=70°
$Ca_2Mg_5Si_8O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$

FIG. 12. Optical properties of calciferous oxyhornblendes.

In other parts of the system data are available to about 60 per cent of the iron molecules.

By such approximate and admittedly unsatisfactory methods the properties of the iron end-members of the calciferous oxyhornblende system have been derived as given in Table 6.

The variations in properties on the front faces of a (partial) triangular prism of the oxyhornblende system are shown in Fig. 11. Finally the variations in properties as related to variations in composition in all parts of the system are shown in clinographic projection in Fig. 12. It is obvious that this is only a first approximation.

In using this graph it should be remembered that it represents the conditions in oxyhornblendes after complete oxidation; many, if not all, natural oxyhornblendes are not completely oxidized; therefore their properties are intermediate between those of ordinary hornblende, and those of completely oxidized hornblende. It may be useful to note that the size of the extinction angle is a guide to the amount of oxidation, but, natural oxyhornblendes with an extinction angle of zero are not completely oxidized (at least in most cases). The size of the optic angle is also a guide to the amount of oxidation, but it can not be measured as easily as the extinction angle.

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THE LOCALIZATION OF COPPER AND SILVER SULFIDE MINERALS IN POLISHED SECTIONS BY THE POTASSIUM CYANIDE ETCH PATTERN

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ABSTRACT

Copper and silver sulfide minerals that are etched by potassium cyanide can be localized in polished sections by contact printing on a lead cyanide emulsion moistened with potassium cyanide. The specificity of the method is studied and conditions formulated for the differentiation of the copper sulfides from other metallic sulfide minerals.

INTRODUCTION

The positive identification of copper sulfide minerals in rock drillings is of importance in economic geology, as these minerals may serve as an index in furthering the exploration of deep seated copper ore bodies. The traces of copper sulfides often occur as minute grains which renders their identification difficult by the standard techniques of ore microscopy.

The methods of contact printing are particularly adapted to the study of minute grains as the mechanical removal of individual micro samples from the surface is avoided. This insures freedom from contamination by particles of non-cupriferous sulfides surrounding or located beneath the polished grain. Also, once a selective printing pattern for a given constituent is devised, the method localizes all identical particles in the polished section. The application of these novel methods of surface analysis in mineralogy have been reviewed by Gutzeit (6) and the diverse printing procedures applicable to the analysis of mineral and biological materials have been classified by Yagoda (12).

Briefly, the printing procedure consists in the dissolution of a thin film from the polished section and its simultaneous transfer to a nondiffusing medium such as gelatin. The ions brought into solution can then be developed for one or more chemical constituents by treating the medium with suitable selective reagents. When the film is stripped with the aid of solvents the developed image is known as a contact print. A large number of the opaque sulfide minerals are good conductors of the electric current. Massive conducting specimens can be stripped electrolytically. This electrographic technique is advantageous in that the flow of positively and negatively charged ions migrating into the gelatin film can be altered by varying the polarity of the specimen. Electrographic methods of analysis are not applicable to minute conducting grains embedded in insulating mounting media or when surrounded by non-conducting gangue minerals.

The copper sulfide minerals most commonly encountered are chalcocite, covellite, bornite and chalcopyrite. Grains of these tracer minerals may be accompanied by other non-sulfide copper minerals such as cuprite, malachite, azurite, chrysocolla, turquoise and native copper. The problem of the identification of the copper sulfide minerals is further complicated by the presence of sulfide minerals of other heavy metals, such as pyrite, sphalerite and galena. In order to identify any given particle as a copper sulfide mineral, there must be a point to point correlation between the copper and sulfide patterns of the polished section.

Satisfactory printing methods are available for demonstrating the presence of copper minerals (5). Difficulties were encountered in obtaining sulfide patterns of the more common opaque minerals utilizing the contact printing methods described in the literature. The method of Baumann (2) utilizing a silver bromide emulsion moistened with 10 per cent hydrochloric acid does not yield a brown silver sulfide print when applied to the common copper sulfide minerals. Likewise, the method of Gutzeit (6) employing 40 per cent hydrochloric acid as the etching agent and antimony trichloride as the indicator failed to yield the characteristic orange colored antimony sulfides when the test was applied as a contact print. In the course of these investigations it was observed that potassium cyanide exhibited a selective solvent action on several members of the copper and silver sulfide groups of minerals and that the sulfide ion liberated by the reaction could be readily fixed in the emulsion by simultaneous precipitation as dark brown lead sulfide.

Mechanism of the Potassium Cyanide Etch

Potassium cyanide dissolves freshly precipitated copper or silver sulfide with the formation of complex salts. The basic reaction is expressed by the following equations:

(1) $Cu_2S + 2KCN \rightarrow 2CuCN + K_2S$

(2) $CuCN + KCN \rightarrow KCu(CN)_2$

This type of complex formation with metallic sulfides is known only for the metals of the first sub-group of the periodic system (Ag, Cu and Au). According to Ephraim (3) thallium and mercury also form complex cyanides which are less stable than those of silver and copper. The stability of the cuprocyanide complex has been utilized as the basis for delicate tests for cyanides by Barnebey (1) and Feigl (4), using freshly precipitated copper sulfide as the reagent. Hiller has described a printing method for the detection of silver sulfide minerals utilizing a mixture of potassium cyanide and the specific silver reagent, p-dimethylaminobenzylidene rhodanine as the etching medium (8). The solvent action of potassium cyanide has also been employed by Hermance (7) in the stripping of sulfide tarnish films from copper and silver alloys.

Potassium cyanide is readily hydrolyzed in aqueous solution with the formation of a high concentration of hydroxide ion. This alkalinity may give rise to side reactions which interfere with the specificity of equations (1) and (2). As a preliminary survey, droplets of solutions of the more common metallic ions were allowed to evaporate on gelatin paper. The sheet was exposed to hydrogen sulfide gas, causing the precipitation of the metallic sulfides. Droplets of 5 per cent potassium cyanide were then placed on the colored sulfides and the solvent action noted: The freshly precipitated sulfides of copper, silver and arsenic dissolved rapidly and completely. Thallium, iron, nickel and cobalt sulfides showed evidence of partial decomposition. The sulfide stains of lead, bismuth, cadmium and antimony remained completely unaltered during a three minute period of contact with the potassium cyanide. These etch reactions on freshly precipitated sulfides indicated that interfering reactions may be anticipated from pulverulent metallic sulfide minerals that are attacked by alkalies.

Method of Obtaining the Potassium Cyanide Etch Pattern

The etching action of potassium cyanide on the copper and silver sulfides is rendered visible as an analytical pattern through the interaction of the potassium sulfide, liberated during the solution process, with a sparingly soluble lead compound incorporated in a gelatin emulsion. The test papers are made by dipping pure gelatin coated paper* for one minute in a 2 per cent solution of lead nitrate. Excess solution is removed by blotting between lintless absorbent paper, and the moist sheets are allowed to dry gelatin face up on a layer of cheese cloth. The supply of lead nitrate paper is then cut into small strips somewhat larger than the size of the polished section. The paper keeps well if stored in an atmosphere free from hydrogen sulfide.

When ready to make a print, a piece of the dry lead nitrate paper is immersed in a 5 per cent solution of potassium cyanide for about 10 seconds, and is moved about in the dish so as to dislodge any adhering air bubbles from the gelatin surface. The paper is drained and all excess fluid removed by blotting between filter paper with the aid of a rubber roller. This process results in the formation of finely divided insoluble lead cyanide dispersed in a gelatin film wetted by excess potassium cyanide.

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* Pure gelatin coated paper free from silver halides can be secured from the Eastman Kodak Co. under the name "Imbibition Paper" or from the Defender Photo Supply Co., Rochester, N. Y., under the designation "Backing S, non-sensitized." A suitable medium can also be made by extracting the silver halide salts from a glossy photographic paper with hypo, washing thoroughly and drying.

The damp freshly prepared emulsion is placed on a soft rubber mat** and the polished section is inclined onto the gelatin surface, so as to avoid the inclusion of air bubbles. The section is pressed against the emulsion and subjected to a pressure of 1 kg. for a period of 1 minute. Those copper or silver sulfide minerals, which are etched by cyanide, are revealed in the print, as mirror images, by the formation of dark brown lead sulfide.

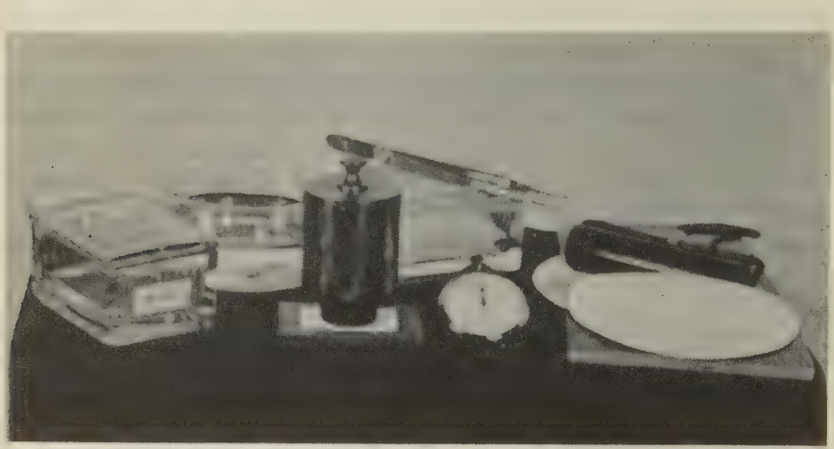

FIG. 1. Apparatus for contact printing.

Center: Polished specimen in bakelite mount in contact with moist emulsion.

Right: Excess cyanide solution removed by blotting between filter paper with aid of rubber roller.

Rear: Staining dishes make convenient receptacles for etching solutions. Test papers are handled with platinum tipped forceps.

The print is washed in water for about 10 minutes to remove soluble cyanides. It is dried by placing the gelatin face down on a glass plate and blotting dry with the aid of a rubber roller. When the paper is thoroughly dry the print springs away from the glass imparting a glossy finish to the gelatin surface. The glass plate should be surfaced occasionally by rubbing with a cloth moistened with a few drops of a 0.1 per cent solution of paraffin in carbon tetrachloride. The paraffin film prevents sticking of the gelatin to the glass.

** This slightly resilient support facilitates perfect contact between the test paper and the polished surface. It is made by cementing a sheet of rubber about 1 mm. thick to a slab of bakelite measuring about $7 \times 5 \times 0.5$ cm.

To facilitate subsequent comparison of the print with the polished surface, it is convenient to make an indicating mark on the cylindrical wall of the mounted section and to orient this mark with the central axis of the paper, as shown in Fig. 1. The dry prints have a tendency to curl. Distortion of the image is avoided by mounting the gelatin paper on a stiff cardboard by means of rubber cement. Typical cyanide etch patterns of massive copper sulfide minerals are reproduced in Fig. 2.

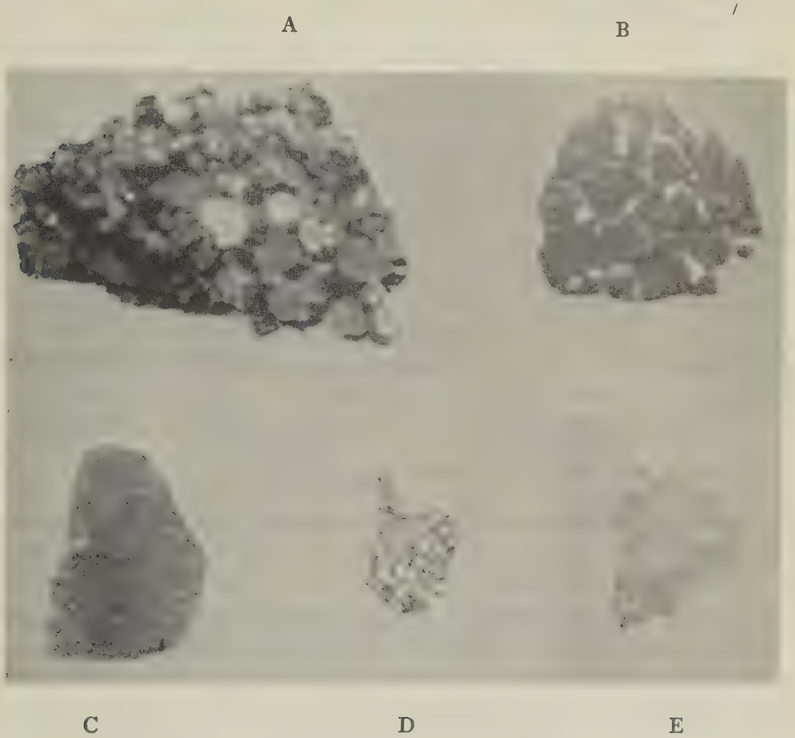

Fig. 2. Sulfide prints of typical copper sulfide minerals.
A: Bornite and chalcocite, Butte, Montana.
B: Enargite, Cerro de Pasco, Peru.
C: Bornite, Bisbee, Arizona.
D: Stromeyerite, Mt. Lyell, Tasmania.
E: Enargite, California (specimen, highly polished).

Response of Sulfide Minerals to Cyanide Etch Pattern

This particular sulfide printing procedure is highly selective. Positive reactions are secured only with those species that are decomposed by potassium cyanide with the liberation of sulfide ion. Table 1 describes the behavior of the common, and several of the available rare members, of the copper and silver sulfide groups. Of the collection of sulfide specimens studied, only chalcocite, covellite, bornite, argentite and stromeyerite give dark brown positive prints. The more complex copper and silver sulfides which contain the As_2S_3 grouping in their structure, as enargite, tennantite and proustite also give positive reactions. The patterns furnished by these minerals, for the identical period of contact, are not quite as intense as in the case of the simple sulfides. When occurring in the same section the two types of minerals can be differentiated by the relative intensity of their prints. A study of Table 1 reveals that in general a good correlation exists between the character of the cyanide etch pattern and the nature of the stain imparted to the polished surface of the mineral when acted on by 20 per cent potassium cyanide. The description of the stains listed in Table 1 are those recorded by Short (11). Minerals which do not stain with 20 per cent potassium cyanide, as chalcopyrite, invariably yield negative sulfide patterns under the conditions of the test.

TABLE 1. COMPARATIVE BEHAVIOR OF MINERALS TO CYANIDE ETCH REACTIONS

Mineral	Composition	Staining with 20% KCN	Sulfide Pattern with 5% KCN
Chalcocite	Cu_2S	quickly stains black	dark brown (3)*
Covellite	CuS	stains black	dark brown (1)
Stromeyerite	$(Cu, Ag)_2S$	quickly stains black	dark brown (2)
Argentite	Ag_2S	stains brown to black	dark brown (3)
Bornite	Cu_5FeS_4	stains brown	brown (2)
Enargite	$Cu_2S \cdot 4CuS \cdot As_2S_3$	stains black	light brown (4)
Proustite	$3Ag_2S \cdot As_2S_3$	stains black	light brown (3)
Argyrodite	$4Ag_2S \cdot GeS_2$	stains light brown	light brown (1)
Tennantite	$5Cu_2S \cdot 2(Cu, Fe)S \cdot 2As_2S_3$	weak or negative	light brown (1)
Tetrahedrite	$5Cu_2S \cdot 2(Cu, Fe)S \cdot 2Sb_2S_3$	weak or negative	negative (2)
Chalcopyrite	$CuFeS_2$	negative	negative (5)
Stannite	$Cu_2S \cdot FeS \cdot SnS_2$	negative	negative (2)

* Number of specimens tested from different localities.

A representative collection of the more common opaque ore minerals was printed by the cyanide etch procedure for possible interfering reactions. The following species gave unambiguous negative tests, the figure in parenthesis showing the number of specimens tested from different localities:

Native Elements: copper (2), silver (2), gold (1), tellurium (2).

Sulfides: stibnite (1), molybdenite (1), galena (3), sphalerite (3), cinnabar (1), pyrrhotite (2), pyrite (3), marcasite (2), realgar (2), millerite (1), ullmanite (2), zinkenite (1), bismutoplagionite (1), jamesonite (1), stannite (2), bravoite (1), tetrahedrite (2), livingstonite (1), chalcopyrite (5), pyrargyrite (1), bournonite (1), cubanite (1).

Arsenides: smaltite (1), niccolite (2), algodonite (1).
Tellurides: rickardite (1), calaverite (1), tetradymite (1), petzite (1).
Selenides: tiemannite (1).

One sample of black sphalerite from Tsumeb, S. W. Africa, gave a strong positive cyanide etch pattern. A confirmatory copper pattern revealed the presence of considerable copper. Schneiderhöhn (10) who has made an extensive study of the sphalerite from this locality concludes that the ore consists of a fine intergrowth of copper sulfides and zinc sulfide.

Polished sections of native copper which had been exposed to laboratory fumes gave a faint stain indicative of a superficial sulfide coating. The freshly polished sections yielded a negative cyanide etch pattern.

Orpiment-As_2S_3 gives an interfering pattern identical in color with those produced by copper and silver sulfides. This reaction is caused by the hydrolysis of the potassium cyanide and the consequent solvent action of the alkali on arsenious sulfide. The more compact realgar-AsS is not etched by cyanide solutions and does not yield an interfering pattern. Orpiment is readily recognized by its characteristic yellow color. The mineral can also be differentiated by the following modification of the contact print procedure. The lead nitrate gelatin paper is moistened with 10 per cent sodium carbonate solution and contacted with the specimen for 1 minute. Orpiment is attacked by the sodium carbonate and yields a brown print of lead sulfide fixed in the lead carbonate emulsion. Sodium carbonate has no solvent action on the copper and silver sulfides, hence they do not print, and the resultant pattern is selective for orpiment.

Violarite-$(Ni, Fe)_3S_4$ is also attacked by alkali and yields a faint greenish brown pattern when contacted against a lead cyanide emulsion moistened with 5 per cent potassium cyanide. Here too the etching is caused by the hydrolysis of the cyanide, as a similar print is obtained when the lead nitrate paper is moistened with sodium carbonate. Short (11, 1st ed., p. 77) describes violarite as unstable and usually crumbly

In the systematic examination of available polished sections for interferences with the copper and silver sulfide pattern, a very unusual color reaction was obtained with an old, surface weathered, specimen from Joachimsthal, Bohemia, labelled "Argentopyrite." Inclusions within the hard massive material yielded a pale blue print. The identical coloration is obtained when pure gelatin paper moistened with 5 per cent potassium cyanide is pressed against the polished surface, indicating that the blue print is formed by the action of the cyanide on a soluble iron mineral. The formation of complex ferro- or ferricyanides is further demonstrated by dipping the pale blue print into dilute hydrochloric acid which causes a marked intensification of the blue color—identical in appearance with Prussian blue. When the specimen is contacted with gelatin paper moistened with *neutral* 10 per cent potassium thiocyanate the inclusions yield a deep red print of ferric thiocyanate. The blue color reaction with potassium cyanide and the red print with potassium thiocyanate has also been observed on some unidentified grains embedded in a massive section of pyrrhotite from Ontario, Canada. These observations are recorded as potential interferences in the detection of copper sulfides, but they also suggest a novel approach in the localization of the native ferric sulphate and ferric chloride minerals.

The native copper and silver selenides are a potential source of interference with the specificity of the sulfide pattern. Short (11) describes the following cyanide etch reactions for the selenide minerals: Aguilarite, $Ag_2(S,Se)$—stains weak brown. Eucairite, $Cu_2Se \cdot Ag_2Se$—instantly stained black. Klockmannite, CuSe—quickly stains black. Umangite, Cu_3Se_2—tarnishes blue. The solvent action of potassium cyanide causes the liberation of potassium selenide, which reacts with the lead cyanide and forms a brown image of lead selenide. The extreme rarity of these species and the difficulty of securing specimens free from accompanying copper and silver sulfides renders their experimental investigation difficult. An ore specimen from Sierra de Umango, Argentina, reported to contain admixed eucairite, klockmannite and umangite furnished a positive brown colored pattern on a lead cyanide-potassium cyanide emulsion.*

The mineral sections employed in these investigations were not polished to a mirror finish. They were simply ground plane on a glass plate with FFF grade carborundum powder. Subsequent comparison of the sulfide prints of ground and highly polished sections showed that for an equal period of contact the polished sections yielded positive prints of lower intensity. Mirror finished mineral surfaces are in general resistant to etching agents. While yielding contact prints exhibiting fine detail in the case of the more readily soluble species, a finely polished specimen may give only a faint or a negative reaction in the case of minerals not readily etched by potassium cyanide as, enargite, tennantite and proustite. These minerals can be printed from highly polished specimens by prolonging the period of contact, or preferably, by dulling the surface on very fine emery paper (grit 4/0) prior to making the print.

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* Preliminary work indicates that the selenides of copper and silver can be differentiated from the more common sulfides by contacting the freshly polished surface against a cadmium ferrocyanide emulsion moistened with potassium cyanide. The selenides yield an orange colored print of cadmium selenide. Sulfides do not react with the insoluble cadmium ferrocyanide.

Differentiation of Copper and Silver Sulfides

The cyanide etch pattern gives positive reactions with chalcocite, bornite, covellite and enargite which are indistinguishable from silver sulfide minerals such as argentite or proustite. In view of the comparative rarity of the silver sulfide minerals, a positive pattern is usually indicative of the more common copper sulfides. However, the members of the two groups can be differentiated by making further contact prints of the polished section and developing these for copper and silver by appropriate selective reagents.

Copper Pattern: Moisten pure gelatin paper with $(1+1)NH_4OH$, blot off excess fluid and contact with polished surface for a period of one minute. Develop paper by immersion in a freshly prepared solution of dithiooxamide of the following composition: Dissolve 100 mg. dithiooxamide in 10 ml. acetone, dilute with 40 ml. methanol and add 1 ml. of glacial acetic acid. Wash print in distilled water and dry. Copper minerals etched by ammonia yield dark olive green prints.

This procedure is a modification of the method described by Niessner (9) for the localization of copper inclusions in alloys, and its application to polished sections of minerals has been described by Gutzeit, Gysin and Galopin (5). Certain nickel bearing minerals which etch with ammonia yield blue prints with dithiooxamide. Likewise, cobalt minerals may yield an interfering brown pattern. Silver minerals soluble in ammonia, as cerargyrite, also yield a brown print on development with dithiooxamide. In general, the olive green markings characteristic of the copper derivative are very distinctive and are readily differentiated from the colors imparted by ammonia soluble nickel, cobalt or silver minerals.

Of the copper sulfide minerals yielding positive cyanide etch patterns, chalcocite, covellite, stromeyerite and bornite yield intense copper prints when etched by ammonia. Enargite and tennantite furnish green prints of lesser intensity. The silver sulfide minerals, argentite, proustite and argyrodite do not print. Chalcopyrite may yield a faint print, but in general, most specimens react negative. Tetrahedrite does not etch with ammonia and therefore yields a negative copper pattern. Certain nonsulphide copper minerals as malachite, azurite, native copper and to a lesser extent cuprite, furnish positive copper prints. The cyanide and copper patterns must therefore be closely examined for proper correlation of points or areas in order to identify a particular grain as a copper sulfide mineral. The high selectivity of the cyanide etch pattern greatly simplifies the examination as only copper or silver sulfides register on the emulsion.

When a given area of the polished section gives a positive cyanide etch pattern for sulfides and the corresponding copper pattern is negative, the mineral may be either orpiment or a member of the silver sulfide group. Orpiment can be identified by inspection and confirmed by etching with sodium carbonate, as previously described. The presence of silver in argentite and stromeyerite can be confirmed by means of the following simplification of the silver pattern originally described by Hiller (8) as an electrographic method.

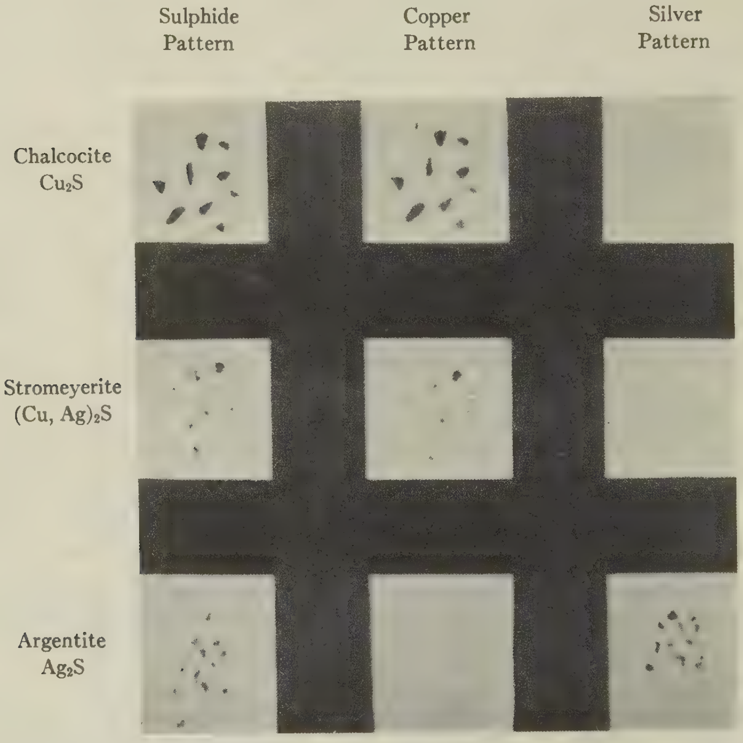

Fig. 3. Differentiation of chalcocite, stromeyerite and argentite by successive analytical patterns.

Silver Pattern: Moisten pure gelatin paper with (1+1) nitric acid, blot off excess fluid and contact polished specimen for one minute. Immerse paper in 2 per cent potassium bromide for about 5 minutes and wash under running tap water for about 10 minutes until the emulsion is substantially free from excess acid and soluble metallic salts. The silver remains fixed in the gelatin as insoluble siver bromide which can be rendered visible by reduction to black metallic silver with the aid of a photographic developing solution.† The print is develped for 3 minutes in full strength *D61a* developer, rinsed with water, immersed in 5 per cent acetic acid for 2 minutes and washed in water for about 15 minutes. Jet black or gray markings on the print serve to localize the silver minerals in the polished section. Native silver and argentiferous alloys such as electrum also yield positive silver patterns.

The application of these contact printing methods in the localization and differentiation of copper and silver sulfide grains is exhibited in Fig. 3. Chalcocite—Cu_2S, stromeyerite—$(Cu, Ag)_2S$ and argentite—Ag_2S yield positive cyanide etch patterns. The chalcocite furnishes a positive copper pattern and a negative silver pattern. Stromeyerite gives positive prints for both copper and silver. The grains of argentite yield a negative copper pattern and a positive silver pattern.

Applications of the Cyanide Etch Sulfide Pattern

The selective sulfide pattern secured by means of potassium cyanide etching is of particular interest in conjunction with the determination and localization of chalcocite, covellite, bornite and enargite in copper ore sections. These particular species are frequently of secondary origin and the occurrence of grains of these copper sulfides in upper rock drillings may indicate the presence of deep seated copper ore bodies. Preliminary analyses of heavy mineral concentrates from rock drillings have demonstrated the applicability of the method in detecting copper sulfide minerals with grains only 0.1 mm. diameter. Details of the mounting of fine grains for contact printing and their identification by successive analytical patterns will be published subsequently.

Copper sulfide minerals occurring in the same section can often be differentiated by noting the relative intensity of the areas on the sulfide pattern. Print *A* of Fig. 2 is a reproduction of the sulfide pattern of a massive copper ore composed of an intergrowth of chalcocite and bornite. The two species are readily differentiated by the dark brown and light brown markings on the pattern. The enclosed crystals of pyrite do not print, but the fine intergrowths of copper sulfide veins within the pyrite are clearly evident in an enlargement print, Fig. 4, of the original pat-

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† Eastman developer *D61a* yields deep black images It is prepared by dissolving 3.1 grams of elon, 90 grams of anhydrous sodium sulphite, 2.1 grams of sodium bisulphite, 5.9 grams hydroquinone, 11.5 grams anhydrous sodium carbonate and 1.7 grams potassium bromide in about 500 ml. of water warmed to 52°C. This is filtered into a stock bottle and diluted with water to 1 liter.

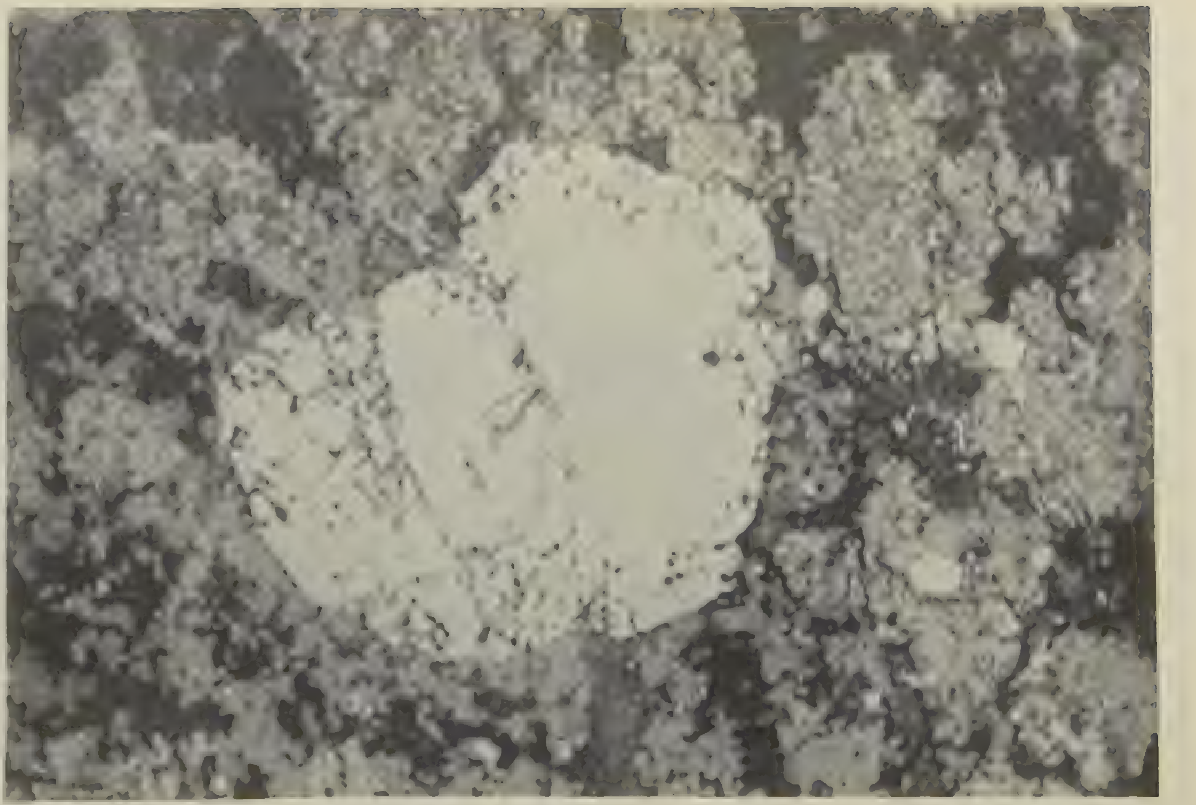

FIG. 4. Fine veins of copper sulfides in pyrite crystal. Pattern enlarged 12 X.

tern. Some of these lines measure between 0.1 and 0.01 mm. in the enlargement, which proves the registration of fine detail on the pattern corresponding to areas with a minimum width of about 0.001 mm. Print *A* of Fig. 5, likewise localizes the copper sulfide areas in a banded intergrowth of enargite and pyrite. The adjacent print *B* is a second pattern of the same section made by contacting the surface for 15 sec. with gelatin paper moistened with (1+1) nitric acid, and developing the print with 2 per cent potassium ferrocyanide. In the original print the enargite areas reproduce reddish brown and the pyrite dark blue. Comparison of the two prints demonstrates that only the enargite furnishes a sulfide pattern.

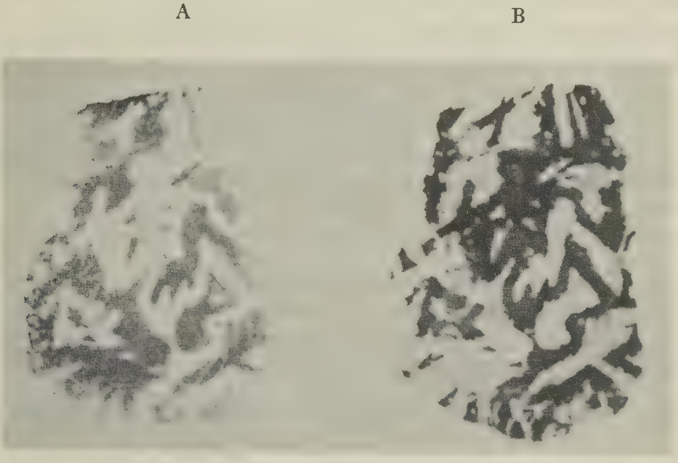

FIG. 5. Banded enargite and pyrite, Cerro de Pasco, Peru

A. Sulfide print of enargite.

B. Combination copper and iron pattern localizing enargite (light) and pyrite (dark).

The simple sulfides such as chalcocite and argentite yield sulfide prints of greater intensity than the more complex species chemically combined with arsenious sulfide. Combinations of copper or silver sulfides with antimony sulfide are not etched by 5 per cent potassium sulfide and yield negative sulfide prints. These characteristics can be utilized in the differentiation of tennantite, $5Cu_2S \cdot 2(Cu, Fe)S \cdot 2As_2S_3$ from its antimony analogue, tetrahedrite, $5Cu_2S \cdot 2(Cu, Fe)S \cdot 2Sb_2S_3$. Likewise, proustite—$3Ag_2 \cdot As_2S_3$ can be differentiated on the print from pyrargyrite—$3Ag_2S \cdot Sb_2S_3$.

ACKNOWLEDGMENTS

This study was initiated at the request of Charles Milton, geochemist at the U. S. Geological Survey, who realized the usefulness of analytical patterns in determinative mineralogy of ore minerals and their applicability to problems in economic geology. The author wishes to thank E. P. Henderson and J. H. Benn of the U. S. National Museum for providing chips of the less common sulfide minerals employed in this investigation. The writer is also indebted to F. A. Lewis and O. Ivan Lee who furnished numerous specimens from their private collections which were employed in the preparation of polished surfaces.

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THE HEAVY MINERALS OF FLORIDA BEACH AND DUNE SANDS

ROSWELL MILLER, III, *U. S. Geological Survey, Washington, D. C.**

ABSTRACT

The identity and proportions of heavy minerals, and in particular rutile and ilmenite, have been determined in a representative collection of beach and dune sands from Florida. The heavy minerals were concentrated by means of heavy solutions, separated into several fractions of varying magnetic properties with a Franz iso-dynamic separator, and proportion determined by means of grain counts. Sixteen minerals were identified, about eight of these (enstatite, epidote, garnet, ilmenite, rutile, kyanite, staurolite and zircon) being present in essential amounts. The so-called ilmenite of these sands proves to be an essentially amorphous material with its iron in the ferric state and hence it is chemically, but seemingly not structurally analogous to arizonite. The size distribution of the quartz sand, and heavy minerals is described in two representative occurrences.

INTRODUCTION

In February 1944 Clarence S. Ross and John B. Mertie of the United States Geological Survey made a field investigation of the rutile-ilmenite bearing sands of Florida. During the course of this investigation, fifteen samples were collected. Other samples were received from C. M. Dunham of Orlando, Florida, and one was collected by Miss Jewell J. Glass of the Survey. The detailed examination of these samples was made by the author in the petrologic laboratory of the Geological Survey in Washington, and throughout the course of the study helpful suggestions were received from Dr. Ross and other members of the Survey. The *x*-ray examinations were made by J. M. Axelrod and the analytical tests by J. J. Fahey, both members of the U. S. Geological Survey.

Two of the localities visited by Ross and Mertie are major producers of rutile, ilmenite, and zircon. The one west of Jacksonville Beach is being operated by a company affiliated with the Titanium Alloy Manufacturing Company, and the one at Vero Beach by the Riz Mineral Company. The samples collected by Ross and Mertie from the Pensacola Bay region were from areas previously investigated by the U. S. Bureau of Mines.

GEOGRAPHICAL DISTRIBUTION

Figure 1 shows the location of the eighteen Florida samples studied in the course of this investigation. They have been arbitrarily numbered from one to ten starting on the east coast with the northernmost location, extending southward down the east coast, thence northward up the west coast, and finally westward to Pensacola. Where a number of samples were collected from one general region it has seemed advisable for the sake of clarity to give them the same number and designate them 4*a*, 4*b*, 4*c*, etc.

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* Published by the permission of the Acting Director of the Geological Survey.

GEOLOGICAL OCCURRENCE

The heavy minerals of the Florida region are very sparse in the areas of Pleistocene sands back from the coast, but occur in noteworthy amounts on the beaches now bordering the shore and in the sand dunes along the coast, and some of these form commercial deposits. On the beaches, wave action has locally concentrated the heavy minerals into discontinuous lenses which range from a mere film to 3 or 4 inches in thickness. On the immediate beach these concentrations change with each recurring storm, and in places heavy minerals may constitute a large percentage of the whole. The heavy minerals in the dune deposits no doubt underwent initial concentration on the beaches, and were later picked up and redeposited by wind action. The proportion of heavy minerals is much lower in the dunes than in some of the richer beach deposits, but the large volume of the dunes makes them a more favorable commercial source of rutile and ilmenite than the beaches. The dunes are of at least two types—modern ones on the immediate coast, and older ones which lie inland at various distances. These old dunes have been reduced almost to the level of the surrounding region, so there is little topographic evidence of their presence. All the present output of rutile and ilmenite is from the old dunes, although in the past the beaches have been productive.

LOCATION OF SAMPLES

The samples included in this study are located as follows:

Sample 1 is modern dune sand collected 4 miles south of Atlantic Beach and 150 yards inland from the beach.

Sample 2 is from ancient dunes 10 miles west of Jacksonville Beach where the sand is being worked commercially. The studies were made on a heavy mineral concentrate from the washing plant.

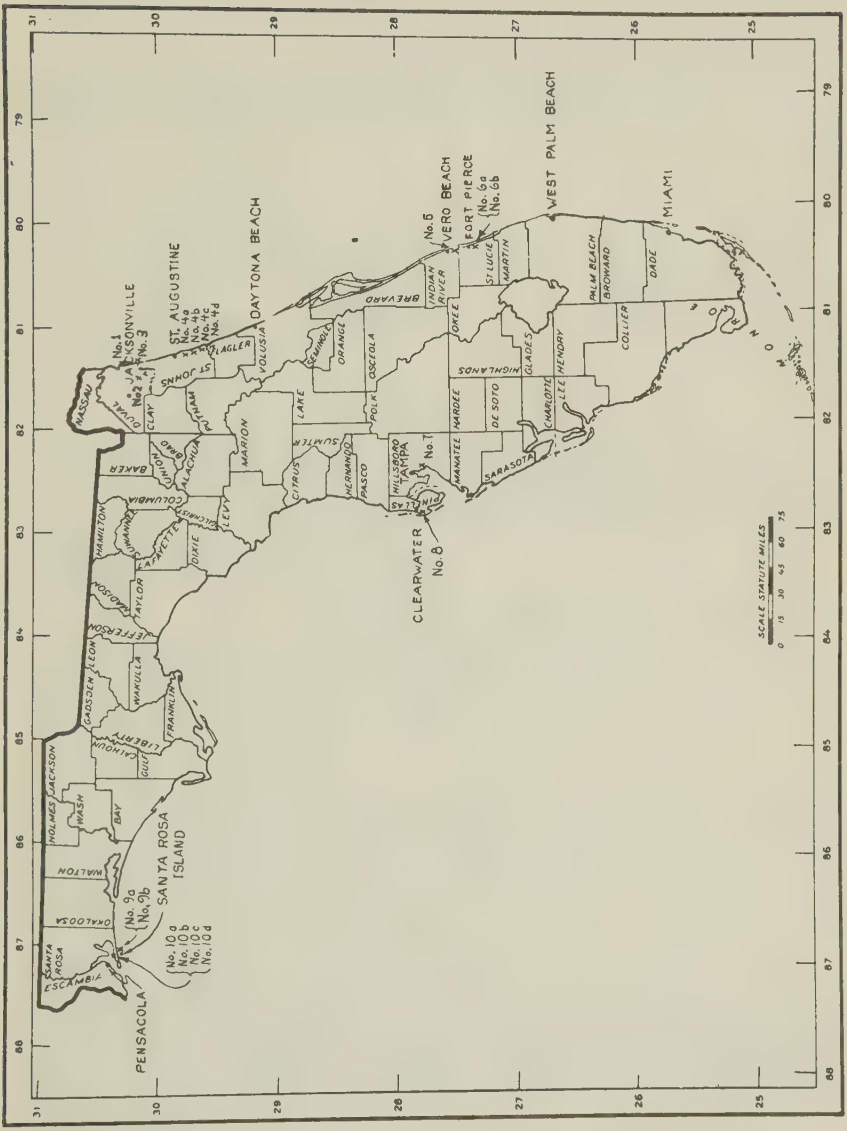
Sample 3 is modern dune sand collected 10 miles south of Jacksonville Beach.

Samples 4*a*, 4*b*, 4*c*, and 4*d* were collected at intervals of 2 to 3 miles starting 4½ miles south of St. Augustine Bridge and extending as far south as the south side of Matanzas Inlet. All four of these samples are wave concentrations found close to the high-tide mark.

Sample 5 is from ancient dunes 3 miles west of the present beach and immediately south of the city of Vero Beach. This material receives initial concentration at Vero Beach, and final treatment at Melbourne.

Samples 6*a* and 6*b* are both from wave concentrates on the beach at Fort Pierce. They were secured through the courtesy of C. M. Dunham.

Sample 7 was collected on the west coast of Florida, from a wave concentrate on the beach just south of Tampa. Sample 7 was also secured through the courtesy of C. M. Dunham.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ORANGE
BREVARD
OSCEOLA
INDIAN RIVER
OKEE
ST LUCIE
MARTIN
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HILLSBORO
PIN
LLAS
MANATEE
HARDEE
DE SOTO
GLADES
HENDRY
CHARLOTTE
LEE
SARASOTA
PALM BEACH
BROWARD
COLLIER
DADE
MONROE
COLUMBIA
HAMILTON
SUWANNEE
GILCHRIST
LEVY
LAFAYETTE
DIXIE
MADISON
TAYLOR
JEFFERSON
LEON
WAKULLA
GADSDEN
FRANKLIN
LIBERTY
CALHOUN
GULF
JACKSON
HOLMES
WASH
BAY
WALTON
OKALOOSA
SANTA ROSA
ESCAMBIA
JACKSONVILLE
No. 1
No 2
No. 3
ST. AUGUSTINE
No. 4a
No. 4b
No. 4c
No. 4d
DAYTONA BEACH
No. 5
VERO BEACH
FORT PIERCE
No. 6a
No. 6b
WEST PALM BEACH
MIAMI
TAMPA
No. 7
CLEARWATER
No. 8
No. 9a
No. 9b
SANTA ROSA ISLAND
No. 10a
No. 10b
No. 10c
No. 10d
PENSACOLA
SCALE STATUTE MILES
0 15 30 45 60 75

FIG. 1

Sample 8 is from a rather sparse wave concentrate on Clearwater Beach.

Samples 9*a* and 9*b* are from wave concentrates taken along the outer beach of Santa Rosa Island, Pensacola, Florida. In this area the wave action is such that concentrates of the heavy minerals changes during each storm.

Samples 10*a* and 10*b* are from Pensacola Bay, Bureau of Mines locality No. 4, reported as situated 9.7 miles west of Camp Navarre.[1] Both samples were taken from thin lamina in the beach sand. Sample 10*a* was collected from the eastern and 10*b* from the western half of the locality.

Sample 10*c* is from Pensacola Bay, Bureau of Mines locality No. 2, 14.2 miles west of Camp Navarre. The material was collected 20 to 30 feet from the water's edge probably at or near high-tide level. The sample was concentrated from two gold-panfuls of sand.

Sample 10*d* is from a wave concentrate from Bureau of Mines locality No. 1 on East Bay, 6 miles south of Milton.

Sample 11 is from a wave concentrate from Scientists' Cliff, Chesapeake Bay, Maryland. This sample was collected by Miss Jewell J. Glass and was studied for comparative purposes.

DESCRIPTION OF THE MORE IMPORTANT MINERALS

Corundum. The sparse corundum grains, as seen under the microscope, are pale blue to colorless in the centers of the grains, bright blue around the edges. The colored parts are faintly pleochroic.

Enstatite. The enstatite is very constant in appearance throughout all the samples in which it occurs. The grains are well rounded, pale brown, and show pronounced cleavage in one direction.

Epidote. The moderately well rounded epidote grains are pleochroic, from almost colorless through pale green to strong green or brownish green. Their index of refraction indicates that they are high in ferric iron.

Garnet. The well-rounded garnet grains are violet pink; they show surprising uniformity, with an index of refraction of 1.80 in most of the grains. In sample 6*a*, however, the garnet has an index of 1.81, in sample 4*a* it varies from 1.80 to 1.81, and in sample 2 from 1.80 to 1.82.These optical properties indicate that the garnets belong to the almandite-spessartite group.

Ilmenite. The material from the Florida beach and dune sands that has commonly been assumed to be ilmenite has essentially the chemical composition of the material that has been called arizonite.[2] It contains about 53 per cent of TiO_2, and its iron is nearly all in the ferric state. Two samples (one moderately magnetic, and the other slightly magnetic) from Vero Beach and one moderately magnetic sample from the locality 10 miles west of Jacksonville Beach were examined by *x*-ray methods.

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[1] War Minerals Report 141, rutile, zircon, ilmenite, kyanite: *U. S. Bureau of Mines*, 1–20 (**1943**).

[2] Palmer, Chase, Arizonite, a ferric metatitanite from a pegmatite near Hackberry, Arizona: *Am. Jour. Sci., Series* 4, **28**, 353–356 (1909).

This examination indicated that all the supposed ilmenite was essentially amorphous, with only weak lines corresponding to ilmenite; hence the material is unlike the type arizonite from Arizona. Thus the relationship of the "ilmenite" of the beach and dune sands, and also of arizonite, needs more detailed study. It is interesting to note that the so-called ilmenite of Travancore is arizonite. On the other hand, x-ray examination of material concentrated from Australian sands indicates that it is ilmenite.

Hornblende. Hornblende is abundant in only one of the sands studied—that is in sample 4*c* from the locality about 10 miles south of St. Augustine. In this sample the hornblende is somewhat variable in color, but most commonly shows pleochroic colors ranging from yellow green or green to blue green. Some of the hornblende shows pale colors, but an essential proportion is nearly opaque in the direction of maximum absorption, has a high index of refraction, and no doubt is high in iron.

Kyanite. The kyanite occurs as large flat grains which are well rounded at the edges. Microscopic examination indicates that they are commonly colorless in the center and blue or green around the edges. With a hand lens the grains are colorless to blue.

Monazite. The grains of monazite are uniformly small and well rounded. They range from colorless to pale yellow brown or greenish brown.

Rutile. Examination with a hand lens indicates that three types of rutile are present in the Florida sands—dull semi-opaque brown, transparent red, and almost black. The red rutile is dominant, the black next, and the semi-opaque brown rarest; any combination of the three may occur in the same sample. The red rutile is usually in crystals or elongate grains, while the other types show no characteristic form. Very intense transmitted light shows that most of the rutile grains that appear black, are in fact very deep red; others are red with some enclosed black pigmenting material. Even the blackest grains are dark red or brown when examined in very finely crushed fragments.

Spinel. The sparse spinel is present in bright green to blue green grains.

Staurolite. The abundant staurolite shows characteristic pleochroic colors ranging from pale reddish brown to dark brown, and commonly contains many inclusions of magnetite. In general the staurolite grains are well rounded.

Tourmaline. The tourmaline, in rounded grains or elongate crystal segments, is pleochroic, its colors ranging from pale brown to dark brown or nearly opaque.

Zircon. Two types of zircon occur in the Florida sands, one being colorless, and the other brownish. The colorless zircon occurs in small euhedral, only slightly abraded crystals, and also in well rounded grains, whereas the brownish zircon is invariably present as irregular rounded grains.

Quartz. The quartz of the Florida sands was not studied in detail, but the unusually pure white sand of the Pensacola area seemed to be a possible source of high-grade glass sand. For this reason a sample of beach sand from Santa Rosa Island, the outermost beach in the Pensacola area, was tested for iron content in the form of Fe_2O_3. The material was first separated in bromoform (sp.g. 2.87), as the grains of iron-bearing minerals form so small a proportion of the Santa Rosa Island sands, that the direct determination of the proportion of iron-bearing minerals by heavy-solution and separation by means of an electromagnet seemed the best method for approximating the iron present in the heavy minerals of the sand. A chemical analysis of an excessively large sample would be required to provide a statistically representative sample. The quartz fraction after removal of heavy minerals was analyzed for iron in the chemical laboratories of the Survey, and the Fe_2O_3 content of the magnetic heavy fraction (composed largely of ilmenite and tourmaline) was estimated as shown below:

Fraction	*Weight percentage*	*Fe_2O_3 percentage*
Light (quartz)	99.968	0.008 (by analysis)
Heavy		
a. Magnetic	0.016	0.005–0.008 (estimated as $\frac{1}{3}$ to $\frac{1}{2}$ of 0.016)
b. Non-magnetic	0.016	mostly kyanite (not analyzed)

From these data it is seen that the total Fe_2O_3 content of the beach sand before removal of the heavy magnetic minerals is between 0.013 and 0.016 per cent, and was 0.008 after their removal.

It is interesting to note that these figures are several times lower than those found by Havell and McVay[3] for the Fe_2O_3 content of the sands of the Mobile area.

The quartz forms an overwhelming proportion of the Pleistocene sand areas of Florida and was not studied in connection with the problem of rutile and ilmenite resources of the state. The proportions of quartz and heavy minerals on the present beaches varies almost foot by foot, and from day to day; therefore, samples collected from areas of local concentration give no adequate idea of the proportion of these minerals in the beach sands as a whole.

The old dune sands, which attain thicknesses of 20 feet or more and represent huge bodies of commercial ore, present a more favorable opportunity for studying the relations between quartz and heavy minerals.

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[3] Havell, R. F., and McVay, T. N., Beneficiation of some Alabama glass sands: *Bull. Am. Ceramic Soc.*, **18**, no. 11, 429–431, Nov. 1939.

TABLE 1. WEIGHT PERCENTAGE OF HEAVY MINERALS IN FLORIDA SANDS

No.	Locality	Occurrence	Apatite	Corundum	Enstatite	Epidote	Garnet	Hornblende	Ilmenite	Kyanite	Magnetite	Monazite	Rutile	Sphene	Spinel	Staurolite	Tourmaline	Zircon
1	4 mi. South of Atlantic Beach	Modern Dune Sand			4	30	2	4	29	2	Tr.		9	Tr.		9	1	8
2	West of Jacksonville Beach	Heads from Washing Plant			24	11	1	1	26	3	Tr.	Tr.	5	1		21	6	3
3	South of Jacksonville Beach	Present Dune Sand	Tr.	Tr.	3	21	2	1	38	3	Tr.		14	Tr.		7	5	7
4*a*	South of St. Augustine	Beach Sand		Tr.	1	8	4	Tr.	38	1	Tr.	Tr.	19	Tr.	Tr.	2	Tr.	27
4*b*	South of St. Augustine	Beach Sand			8	24	1	3	34		Tr.		14	Tr.		2	2	12
4*c*	South of St. Augustine	Beach Sand			12	44	Tr.	15	19	Tr.	Tr.		6			Tr.	5	Tr.
4*d*	Matanzas Inlet	Beach Sand		Tr.	3	3	8		51	2	Tr.	Tr.	15		Tr.	5	1	10
5	Vero Beach	Rough concentrate Melbourne Plant		2	2	3	2		36	1	Tr.	Tr.	27	Tr.		20	Tr.	6
6*a*	Fort Pierce	Beach Sand		Tr.	2	4	3		26	Tr.	Tr.		24	Tr.		28	1	12
6*b*	Fort Pierce	Beach Sand		1	3	Tr.	Tr.	Tr.	28	Tr.			28		Tr.	27	2	10
7	Tampa	Beach Sand			5	3	5	Tr.	26	8		Tr.	22	Tr.	Tr.	14	2	15
8	Clearwater	Beach Sand				1	17	1	23				1			47	10	1
9*a*	Santa Rosa Is.	Beach Sand		Tr.	1		Tr.		15	12			7	Tr.	Tr.	18	2	43
9*b*	Santa Rosa Is.	Beach Sand		Tr.	1		Tr.	Tr.	19	45	Tr.	Tr.	9	Tr.	Tr.	22	5	Tr.
10*a*	Pensacola Bay	Beach Sand			1			Tr.	14	35	Tr.		16		Tr.	29	1	4
10*b*	Pensacola Bay	Beach Sand			Tr.			Tr.	9	40	Tr.		8	Tr.		38	2	1
10*c*	Pensacola Bay	Panned Beach Sand			1				8	35	Tr.	Tr.	5	1		40	2	9
10*d*	Pensacola Bay	Beach Sand			Tr.				23	30	Tr.	Tr.	7	1	Tr.	34	3	2
11	Chesapeake Bay, Maryland	Beach Sand		Tr.	1	Tr.	3		39	1	25		11	Tr.	Tr.	11	Tr.	8

At the locality about 10 miles west of Jacksonville Beach, the proportion of heavy minerals was determined in three samples. A low-grade white sand near the bottom of the deposit contained 6.14 per cent of heavy minerals. Two more representative samples contained 12.1 and 19.2 per cent, respectively. The ilmenite in these 3 heavy fractions amounted to 1.6, 3.3, and 4.2 per cent, and the rutile 0.3, 0.6 and about 1.0 per cent of the entire samples.

The quartz from the old dune deposit about 10 miles west of Jacksonville Beach is sub-angular to sub-rounded in shape, but is very rarely well rounded. The sands from the old dune at Vero Beach are sub-rounded, with many more well rounded grains than in those at the locality west of Jacksonville Beach. The modern beach sand from the locality 10 miles south of St. Augustine is sub-angular to sub-rounded with well-rounded grains very rare. The sand from Santa Rosa Island is the coarsest-grained sand examined, as nearly all of the quartz grains range between 0.6 to 0.3 millimeters in diameter (between 28 and 6 meshes per inch). The grains are sub-rounded to well rounded in form.

DISTRIBUTION OF MINERALS

The accompanying table shows the percentages of the minerals in the heavy-mineral fraction of each sample examined. From its study definite trends may be observed in the occurrence and abundance of some of the minerals in relation to the geographic location of the samples. These trends will be pointed out for the individual minerals and then discussed in relation to one another.

Enstatite. The distribution of enstatite is highly irregular, but in general the mineral is less abundant in the Santa Rosa Island and Pensacola Bay samples than elsewhere.

Epidote. Epidote shows the same trend as enstatite, but more emphatically. It is abundant on the north part of the east coast as far south as St. Augustine, becomes decidedly scarcer farther south along the east coast and in the Tampa area, and disappears entirely in the Pensacola Bay area.

Garnet. The percentage of garnet in the Florida beach and dune sands is extremely variable. On the east coast it is present in quantities ranging from a trace to 8 per cent of the heavy minerals. On the west coast at Clearwater Beach it reaches its peak of 17 per cent, but on Santa Rosa Island it drops back to a trace. No garnet was found in any of the four samples from Pensacola Bay.

Hornblende. Only one sample, that from about ten miles south of St. Augustine shows a noteworthy amount of hornblende.

Ilmenite. "Ilmenite" is irregular in abundance but shows a drop in quantity in the Pensacola Bay and Santa Rosa Island localities.

Kyanite. This mineral is a very minor constituent in all the samples with the exception of those from the Pensacola Bay area where it is very abundant. In this area the lowest percentage of kyanite, 12 per cent in one of the Santa Rosa Island samples, is more than four and one-half times as great as the highest percentage of this mineral in any one of the other samples.

Magnetite. Magnetite is rare in all the Florida sands and shows no observable distribution trend. In contrast, the sample from Chesapeake Bay, Maryland, is high in magnetite, whose abundance indicates that this sand is much nearer its source than are the Florida sands and has undergone a minimum of oxidation.

Rutile. The proportion of rutile in the sands shows a tendency to vary directly as the ilmenite. On the east coast epidote and rutile tend to vary inversely, while in the same region the ilmenite is abundant but variable. Sample 4*c*, however, is an exception inasmuch as both the rutile and ilmenite decrease in abundance while the epidote increases to 44.2 per cent.

Staurolite. With the exception of sample 2, staurolite shows a tendency to decrease on the east coast as far south as Matanzas inlet. In the next sample, from Vero Beach, its percentage rises sharply and it is fairly to very abundant in the remainder of the samples.

Zircon. No trends are evident in the distribution of zircon in the various samples; however, at both St. Augustine and Santa Rosa Island extreme variations in the zircon content of the sand occur within comparatively short distances. The mineral is subject to intense local concentration rather than a gradual concentration over a large area.

The significance of these trends is not altogether clear. A larger number of samples would have served to counterbalance the effects of local conditions of concentration. The study of many more samples collected at reasonably regular intervals over the whole coast line would have been highly desirable. The samples studied, however, disclose the characteristic heavy minerals in areas so far from the crystalline source rocks that transportation over long distances and repeated reworking have eliminated all but the most resistant materials. The study also shows the essential proportions of economically important minerals, rutile, zircon, and ilmenite in an area that is a major source of these essential minerals.

GRAIN SIZE

Time did not permit complete analyses of grain size in all the samples; however, samples 3 and 5, which represent the two sands of present commercial value, were screened and their grain sizes were plotted against the weight percentage, as shown in Figs. 2 and 3. In both figures the percentages of different grain sizes of the heavy minerals and of the

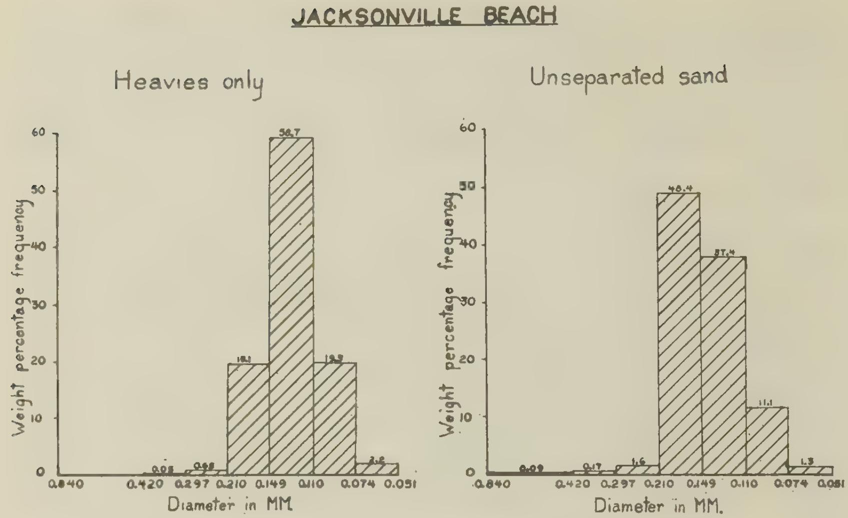

FIG. 2

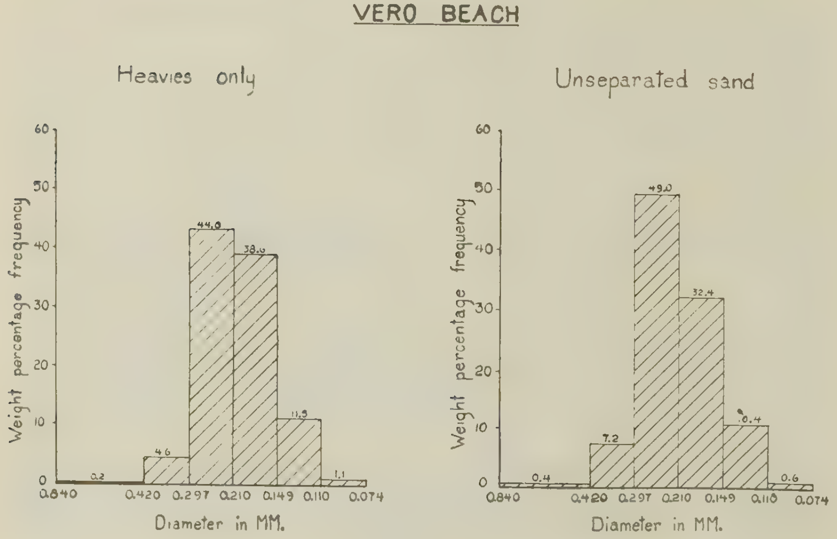

FIG. 3

unseparated sand are represented by diagrams. Comparison of the diagrams representing heavy minerals and unseparated sand shows that at both localities the quartz occurs in coarser grains than do the heavy minerals; also that the Jacksonville Beach sand is not only finer grained than the Vero Beach sand, but is also much more regular in grain size. In the heavy minerals of the Vero Beach sample 98.7 per cent of the grains are between 0.420 mm. and 0.110 mm. in diameter—an interval of 0.310 mm. In the unseparated sand 99.0 per cent of the grains lie within this interval. At Jacksonville Beach 97.1 per cent of the heavy minerals and 97.9 per cent of the unseparated sand has a diameter of 0.210 to 0.074 mm., an interval of 0.136 mm.

Laboratory Procedure

Each sample was first treated with dilute hydrochloric acid (1:1) to remove all carbonate material. This also removed collophane where it was present. The heavy minerals were then separated from the quartz in bromoform. Next, the heavy minerals were magnetically separated into three fractions with a Franz iso-dynamic separator. the magnetite having been removed first with a hand magnet. The presence of opaque rutile caused some difficulty, but it was found by experimentation with commercial concentrates that both the opaque and non-opaque rutile could be separated from the ilmenite by using a current of 0.45 amps in the separator; consequently, the first magnetic separation of each sample was made at 0.45 amperes, all the opaque material in the magnetic fraction being recorded as ilmenite and all the opaque material in the non-magnetic fraction being recorded as rutile. The essential correctness of this assumption is confirmed by the titanium content (92 per cent or over) of the commercial concentrates, which are essentially similar to the concentrates made in this laboratory.

The non-magnetic fraction at 0.45 amps was then separated by using 1.4 amps, thus dividing the heavy minerals into three fractions. Each of the fractions was then studied microscopically, the minerals identified, and grain counts made. Approximately 500 grains were counted in addition to any contaminating minerals. After grain countings, corrections were made for specific gravity of each mineral and the weight percentages calculated.

NOTES AND NEWS

ZUNYITE IN UTAH*

T. S. LOVERING† AND BRONSON STRINGHAM‡

Unusually fine zunyite has recently been found in the Tintic district of Utah. The material was brought to us for identification by Mr. Lee Armstrong of the Longyear Drilling Company and was obtained from the Mintintic property about a mile and a half south of Silver City. It occurs along a steep northeasterly fissure, both as a fissure filling and as an impregnation of the silicified tuff that makes up the country rock. Some well crystallized iron stained zunyite forms a vein about four inches wide but much more is present in the walls of the fissure. Associated with the zunyite are rutile, alunite, dickite, octahedral pyrite, and two generations of quartz, all earlier than the zunyite.

The average size of the crystals of zunyite is about 2 mm. but crystals $4\frac{1}{2}$ mm. across are present locally in the vein. They appear as brilliant phenocryst-like tetrahedral individuals lying in a moderately soft brownish porous matrix whose color and porosity are probably due to oxidation of associated pyrite. Nearly all crystals have well developed positive and negative tetrahedrons $\{111\}$, $\{1\bar{1}1\}$, and the cube $\{100\}$. Small fragments are water clear but most crystals appear light brown because of the iron oxide that stains the surface and internal fractures. Small inclusions of quartz are present in all the zunyite studied so neither the specific gravity nor chemical composition were determined.

Excellent zonal growth with a very slight variation in indices of refraction was observed in thin section. Usually the outer zone had the highest index of refraction with a nearly constant value of 1.596; that of the inner zones was moderately variable, commonly ranging between 1.595 and 1.594. The index did not rise progressively from core to rim but instead zones of higher and lower index alternated or showed an unsystematic variation.

Spencer (1930) suggested that the variation in the indices of refraction of zunyite might be due to a change in the fluorine-hydroxyl ratio, the index dropping with decreasing fluorine and increasing hydroxyl. However, a comparison of the recorded analyses shows that both hydroxyl and fluorine are very constant, except for the zunyite from South Africa. Moreover the index of the material with less hydroxyl is lower than that of zunyite containing the higher proportions of hydroxyl. We conclude that available data indicate that the variation of indices is most closely related to the fluorine-chlorine ratio, and that the index rises with increasing chlorine and decreasing fluorine.

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The index of the Mintintic zunyite correlates it with the high fluorine zunyite found in the type locality in Colorado.

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NOTES ON CEMENT-AGGREGATE REACTION IN CONCRETE

Duncan McConnell and William H. Irwin*

During the past few years, engineers, including some who are among the leaders in design and construction of concrete structures, have become convinced that the rocks and minerals used as concrete aggregates are not chemically inert as had been more or less tacitly assumed during earlier decades. The concept of cement-aggregate reaction has been considered with increasing interest wherever engineers associate, and numerous publications on the subject have made their appearance in the engineering literature.

In this brief note, it is not intended to discuss the fundamental principles involved in the interaction between cement and aggregate, although some reasonable theories have already been proposed; it is the intention of these comments merely to call to the attention of mineralogists and petrographers an important engineering application of their science.

During the summer of 1941, the Bureau of Reclamation, having become adequately convinced of the deleterious nature of interactions between some aggregates and cements containing more than 0.6 per cent of alkalies (soda plus the sodic equivalent of potassa), greatly extended the facilities and staff of its Petrographic Laboratory. One of the foremost duties of the laboratory staff was an investigation of the causes, effects, and preventative measures of cement-aggregate reaction. The results of some of these investigations will appear in the near future.

Experience has proved that several types of natural aggregate materials are capable of interaction with the alkaline solutions which persist in cement paste subsequent to set of the concrete when high alkali cements are employed in the mix. Most reactive are opal-bearing rocks of all sorts, but certain glassy volcanic rocks of acid to intermediate compositions and certain chalcedonic rocks (including some cherts) behave in a similar manner although possibly to a lesser degree. In addition to the forenamed rocks containing glasses or hydrated silica, some phyllites and/or low grade schists also furnish conclusive evidence of reactivity. In this instance the reactivity may be associated with the occurrence of large quantities of hydromicas in the phyllites; however, rocks of this sort are known to have caused difficulty in only a few cases and for this reason a more thorough investigation of the reactivity of phyllites has not been undertaken to date.

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Evidences of cement-aggregate reaction become manifest through several phenomena: unsightly cracking on the surfaces of concrete structures, exudation of gelatinous deposits, etc. The most alarming effects from the engineering standpoint, however, are the expansion and deterioration in strength of the concrete. In some instances, these effects may become so serious as to necessitate extensive repairs or replacements.

TABLE 1. EXPANSIONS OF LABORATORY MORTAR BARS FABRICATED WITH HIGH ALKALI CEMENT

(Various Reactive Aggregates Substituted for Quartz)*

Substituted material			Expansions in per cent	
	Size	Per Cent	6 months	12 months
Vein quartz, Colorado	G	—	.025	.033
Rhyolites and Andesites, Parker Dam	8	19	.280	.398
Andesites, Friant Dam	G	100	.262	.371
Acid Volcanics, Kimball, Nebraska	G	100	.519	.665
Cherts, Kimball, Nebraska	G	100	.757	.863
Novaculite, Arkansas	G	75	.499	.537
Obsidian, Lake Co., Oregon	G	75	.065	.261
Pitchstone, Colorado	G	50	.561	.699
Opaline shale, California	30	4¾	.867	1.655
Opal, Nevada	G	5	1.723	2.218
Phyllite, Virginia	8	19	.095	.201
"Pyrex" (glass)	G	50	.841	.874
Alunite, Utah	G	5†	.832†	1.351†

* All bars contained 1 part cement to 2 parts aggregate (by weight); aggregate was graded according to sizes; bars were cured in a moist atmosphere at 100° F.; cement No. 2742 (Na_2O 1.30, K_2O 0.12). Combinations indicated by "G" in the second column contained 20 per cent of each size from No. 8 to No. 100 sieve and substitutions were made for all sizes; otherwise the test material was substituted for equal quantities of quartz for the size shown.

† Expansions are shown only for 5 per cent substitution because bars containing large amounts of alunite expanded beyond the range of the comparator at early ages.

(All data obtained in the laboratories of the Bureau of Reclamation, U. S. Department of the Interior, Denver, Colorado.)

Although the field service history of concrete is the ultimate basis for judging its quality, laboratory test bars frequently provide valuable information on expansive potentialities. One of the early phases of the Bureau's program of investigation consisted of preparing mortar bars with numerous common minerals likely to occur in many natural aggregates. These minerals included quartz, feldspars of several compositions, the commoner accessory minerals of igneous rocks, etc. Without exception the primary minerals of phaneritic igneous rocks showed insignificant expansions when used with high alkali cement in the fabrication of mortar bars. Comparative data on the expansions of several of the more reactive aggregates are shown in Table 1.

Typical reactive aggregates contain silica and/or silicate minerals and show significant expansions only when high alkali cement is used. An interesting example of a mineral that reacts with both low and high alkali cement is alunite, the behavior of which might have been predicted from its composition and the presumption of its attack by cement solutions. Sulfate-bearing solutions have long been known to cause destructive attack on concrete, and thus it is not particularly surprising that this mineral should produce extreme expansion (Table 1) and distortion of laboratory bars. Fortunately however, alunite is not known to occur in significant quantities in any natural aggregate.

Volcanic rocks are particularly abundant in the western portions of the United States and have furnished numerous examples of reactivity as aggregates. However, the occurrence of reactive cherts, opal-bearing rocks, and reactive phyllites in other regions of the country cannot be safely ignored. These several examples serve to emphasize the importance of the mineralogical and petrographic study of concrete aggregates.

THE DESTRUCTION OF THE LIÉGE MUSEUM

J. D. H. Donnay, *Hercules Powder Company, Experiment Station, Wilmington, Delaware.*

> *"... les minéraux cristallisés, je les aime à cause de leur transparence ou de leur éclat, de leurs belles couleurs si variées et de leurs formes si harmonieuses, si caractéristiques et souvent si compliquées en apparence."*
>
> *G. Cesàro*
> (*Jubilee Speech, July 16, 1929*)

A short letter, dated October 23, 1944, has just been received from Professor H. Buttgenbach, Director of the Mineralogical Museum of the University of Liége, Belgium. The following statement is quoted from this letter: "*The whole museum (except for a few pieces which were in the vault) and all the other facilities were burned the day the Germans left! It is a great disaster.*"

All lovers of minerals will be stunned by the shocking news and will share the grief of their Belgian colleagues. Rare and well crystallized specimens, patiently accumulated for over a century, things of beauty, many of them irreplaceable, are lost forever.

Professor Buttgenbach had published a brief history and a description of his museum shortly before the war (1938). He recounts that the University of Liége was founded in 1817 and that a course in mineralogy was offered from the very beginning. H. M. Gaède was the first professor; he formed the nucleus of the collection. For two years (1828–30) the French crystallographer A. Lévy taught at Liége. His system of form notation, modified after that of Haüy, is still used, jointly with Miller indices, in French publications. He assembled a large collection of minerals from the famous Moresnet district, where he found the "new" species *willemite* six years after Vanuxem and Keating had reported a "siliceous oxide of zinc" from New Jersey, in the *Journal of the Philadelphia Academy* (1824). Lévy is also remembered for his work on the Heuland Cabinet, and his name was given by Brewster to a zeolite of the chabazite group (*lévyne*).

The great geologist André Dumont, who, while still in his teens, had shown "that the order of superposition of strata, as found in the field, is not necessarily the order of deposition," taught mineralogy and geology from 1835 to 1857. He contributed more than 3500 specimens to the museum. His name lives in the mineral *dumontite*. He was succeeded by another geologist, G. Dewalque (1857–91). A mineral was named *dewalquite*, but is now generally known as *ardennite* for reasons of priority.

Dewalque chose as his successor a man without any university degree, but who was to become the shining light of the Institute of Crystallography and Mineralogy, G. Cesàro. The latter lectured from 1891 to 1921 and kept up a steady flow of contributions for half a century, until 1939, when he died at the age of 89. He gave a strong impulse to crystallographic studies; his most celebrated memoir is probably his description of the calcite crystals from Rhisnes, Belgium. *Cesàrolite,* a lead manganate, was named after him by the present incumbent, Professor H. Buttgenbach, who has occupied the chair since 1921, and whose own name is recalled by a mineral from the Congo, *buttgenbachite.* Other members of the Liége faculty took an interest in the museum and fostered its development. The names of many of them have been given to minerals—Davreux, de Koninck, Lohest, Destinez, Fraipont, and Fourmarier.

New mineral names that originated at Liége include, besides *willemite* and *cesàrolite* already mentioned, *delvauxine*, *salmite*, *fraipontite*, *richellite*, *cornetite*, *destinezite*, *lohestite*, *sharpite*, *katangite*, *fourmariérite*, *droogmansite*, and *berthonite.* The new minerals from the Belgian Congo have been studied principally by Professor Buttgenbach, who described several of them.

In 1937 the collections were moved to a new building, a former bank, especially well suited for the purpose. The show-cases were housed in the main concourse, under a high glass roof, which flooded them with sky light. The following year, the Ungemach Collection, of Strasbourg, France, famed for the quality of its crystallized material, was added. At about the same time, Professor Buttgenbach donated his personal collection, which had been housed in Brussels up to then.

Last summer, before the disaster, the Mineralogy Museum comprised over 32,000 specimens, distributed as follows. (1) The Systematic Collection, over 21,000 specimens belonging to 831 different species. (2) The Collection of Minerals from Belgium, over 4500 specimens representing the 114 species found in that small country. (3) The Collection of Minerals from the Belgian Congo, 360 specimens representing 138 species. (4) The Ungemach Collection, over 6000 specimens, stressing the variations of crystal habit from locality to locality. (5) The Cesàro Type-Material Collection, comprising all the crystals which Cesàro studied and described in his publications; for instance, the Belgian calcite crystals and the minerals from Vesuvius and Monte Somma. (6) Several Special Collections, mainly of didactic interest, illustrating twinning, mineral associations, pseudomorphs, gem minerals, synthetic gems, igneous rocks, and meteorites (four falls in Belgium were represented). Also worthy of mention was an excellent collection of more than 850 wooden models, showing the habits of individual minerals. Every one of the specimens was carefully indexed. As Professor Buttgenbach proudly stated in his description of the museum, "I have made it a point to prepare a complete catalogue, on filing cards, so that we know exactly what we possess."

Now the Liége Mineralogical Museum, sharing the fate of the historic Law Courts, is a charred heap of rubble. Gone, the unique heterobrochantite. Gone, the beautiful kipushite. Gone, the rare Moresnet hopeite of 1826. Gone, the exquisite ruby silvers of Ungemach. Gone, the Rhisnes calcites. Gone, all of them! Destroyed—along with Ungemach's goniometer, the keepsake which his children had presented to the Institute, along with the microscopes, the refractometers, the books, the laboratories, the offices, the shop—and the catalogue. Today, Professor Buttgenbach and his associates, Messrs. Mélon and Bailly, no longer need their complete catalogue, with its thousands of cards, to know exactly what they possess.

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BOOK REVIEW

THE PHOTOGRAPHY OF THE RECIPROCAL LATTICE by M. J. BUERGER. ASXRED MONOGRAPH NO. 1. Published by the American Society for X-ray and Electron Diffraction. ix+27 pp., 18 figs. Copies may be obtained from the Murray Printing Company, 18 Ames St., Cambridge 42, Mass. Price $1.50.

This monograph describes a method of photographing the reciprocal lattice which is based upon the geometrical principles of de Jong and Bouman for obtaining undistorted projections of the reciprocal lattice, combined with a precessing motion of the crystal, first described by the author in his "X-ray Crystallography." The method is consisely but clearly presented, and the underlying theory, the apparatus design, and the types of photographs secured are well illustrated.

Interpretation of the photographs is comparatively simple, since they are scaled photographs of individual lattice levels. Thus the method is of special value for crystals with very large unit cell dimensions. In setting the apparatus for *n*-level photographs, each precession photograph contains a measure of the error in the reciprocal lattice value used. The method can be used to locate a rational axis in an unoriented crystal fragment. Exposure times for regular exposures are short, and for orientation, exposures of a few minutes suffice for correction purposes. Perfection of the crystal is required only for a very small cylindrical volume through the crystal; possible adjacent twinned or distorted areas do not enter the *x*-ray beam. Compared with the Weissenberg method, less of the reciprocal lattice is recorded, and *n*-level photographs lack a record in the center.

L. S. RAMSDELL

PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences of Philadelphia, September 7, 1944

The vice-president, Mr. Charles R. Toothaker, was in the chair, with 62 members and visitors present.

Dr. Richard E. Stoiber of the Quartz Crystal Section of the OCSigO, War Dept., addressed the society on "Quartz Crystals in Brazil." The quartz belt extends from northern Bahia to central Minas Geraes and covers hundreds of square miles. The typical mode of occurrence is at the contact of granite and red shale, where crystals are found locally in pockets associated with milky quartz and black manganese oxide. Geological features of the deposits and mining methods were illustrated with kodachrome slides.

Mr. Samuel G. Gordon exhibited an etched X-section of quartz which showed the rare case of "Combined" twinning, in which the right and left individuals are reversed, rather than the usual case of an intergrowth of an enantiomorphous pair ("Brazil twinning"). He pointed out that the latter type of twinning is as common in quartz as polysynthetic twinning in plagioclase.

October 5, 1944

Dr. W. Hersey Thomas presided, with 48 members and visitors present. The present officers were reelected.

Dr. Earl Ingerson of the Geophysical Laboratory spoke on "Interpretation of Preferred Orientation of Minerals in Rocks." Methods of plotting preferred orientations in thin sections of rocks were described, and geological applications were illustrated.

Mr. Gordon reported on a trip with Mr. Horace Hallowell to the quarry at Branchville, now being worked for mica, but only albite and tourmaline were collected. Mr. Harold Evans exhibited four trays of cut stones.

November 2, 1944

Dr. W. Hersey Thomas presided, with 100 persons present, following a dinner in honor of the guest, Dr. Charles Palache.

Professor Palache addressed the society on "The Genesis of the Zinc Deposits of Franklin, N. J." He described his first trip to that locality in 1896, as well as his impressions of the collections of Canfield and Hancock. The main deposits are considered to represent zinc sulfides which have been thoroughly oxidized to hemimorphite, and then subjected to metamorphism. The local effects of pegmatites and hydrothermal solutions in the development of rare minerals (many of which had been placed on exhibition) was alluded to. The talk was illustrated with maps and photographs reproduced as lantern slides.

December 7, 1944

Dr. W. Hersey Thomas was in the chair, with 63 persons present.

Dr. Hugh Miser of the U. S. Geological Survey addressed the society on "Quartz Crystals and Veins in Arkansas." While veins of quartz occur in a belt 30 to 40 miles wide, and 150 miles long from Little Rock, Arkansas, to Broken Bow, Oklahoma, the quartz crystal producing area is limited to the main anticlinorial axis of the Ouachita Mountains, where upwarping developed cracks in the crest of the anticlinorium. Through these cracks flowed hot hydrothermal solutions of magmatic origin which deposited the quartz crystals. The hydrothermal origin of the quartz crystals is proven by the associated dickite, calcite, and adularia. The late Paleozoic age of the quartz veins is shown by the entire absence of any veins in the Cretaceous rocks (in fact quartz veins are cut by Cretaceous igneous dikes), and also by the great quantity of rolled quartz pebbles found in the Cretaceous sedimentary beds.

The relation of the quartz veins to the veins of lead, copper, zinc, and mercury in the Ouachita and Ozark Mountains was described, and a Pennsylvanian age was shown for these, and a similar age was suggested for the lead-zinc deposits of the Tri-State area and similar deposits in the Mississippi Valley.

A remarkable group of milky quartz crystals from Berkeley Springs, West Virginia, and weighing several hundred pounds, had been presented to the Academy by Mr. George D. Cope, and was exhibited.

Dr. Joseph D. H. Donnay suggested that a committee be appointed to help replace the collection of minerals destroyed at the University of Liége by the retreating Germans.

J. S. Frankenfield, *Secretary*

ABSTRACTS OF THE MINUTES OF THE NEW YORK MINERALOGICAL CLUB

Meeting of October 19, 1944

The president, Mr. Taylor, announced the appointment of the curators' committee and committees in charge of excursions, membership, auditing, programs, education and publications. The meeting was open for accounts of summer collecting by the members. A five-inch scalenohedral calcite crystal from the Prospect Park quarry at Paterson, N. J., was exhibited by Mr. Leonard Morgan who had collected it. Other exhibits included agates from the north shore of Long Island and from streams near Summit, N. J., and corundum sent by a member of the armed forces on duty in South Africa.

Meeting of November 15, 1944

The Vice-president, Dr. R. B. Sosman, reviewed the first volume of the new edition of Dana's *System of Mineralogy* and the president called attention to *Bulletins* **50** and **57** of the New Jersey State Department of Conservation. Mr. George Ashby presented to the club a volume representing his work on the inclusions in mica found on Manhattan Island from 1900 to 1925. Dr. William Parrish addressed the club on "Isomorphism and Polymorphism," illustrating his talk with numerous specific examples among minerals.

Elizabeth Armstrong, *Secretary.*

NEW MINERAL NAMES

Banalsite

W. Campbell Smith, F. A. Bannister, and M. H. Hey: A new barium-feldspar from Wales. *Nature*, **154**, No. 3906, 336–337 (1944).

Name: From the formula.

Crystallography: Orthorhombic, with unit cell dimensions a 8.50, b 9.97, c 16.73 Å., space group $I\ b\ a$ or $I\ b\ a\ m$. The unit cell contains 4 $BaNa_2Al_4Si_4O_{16}$. No crystal forms were visible on hand specimens but thin sections showed indications of a few faces of simple indexes including {110} and {001}, both parallel to good cleavage directions. The unit cell has dimensions similar to those of sanidine.

Chemical Properties: Microchemical analysis (not given) gives the formula $BaNa_2Al_4Si_4O_{16}$

Physical Properties: White. $D_4^{16}=3.06$. Optically positive, $\alpha=1.5695$, $\beta=1.5710$, $\gamma=1.5775\pm.005$ (Na light); $2V=41°$, $\alpha=c$, optic axial plane parallel to {100}

Occurrence: Banalsite occurs massive, associated with tephroite, alleghanyite, jacobsite, barite and calcite in certain rare veinlets and narrow bands in dark purple manganese ore from the Benallt mine near Rhiw, Carnarvonshire, Wales.

Michael Fleischer

Yenerite

J. v. Steiger and O. Bayramgil: Yenerite, ein neues Blei-Antimon-Sulfosalz aus Işikdağ (Turkei). Abstract in *Schweiz. Mineralog., Petrog. Mitt.*, **23**, 616 (1943.)

Name: Origin not stated.

Chemical Properties: Analysis gave Pb 57.32, Sb 23.60, As 1.83, S 17.06, Cu trace, Fe trace; sum 99.81%. This corresponds to $11PbS\cdot4Sb_2S_3$, intermediate between boulangerite, $10PbS\cdot4Sb_2S_3$, and falkmanite, $12PbS\cdot4Sb_2S_3$.

X-ray Data: A rotation photograph around the needle axis gave 8.05±.05 Å. as the identity period parallel to this axis. The powder pattern shows great similarity to those of boulangerite and falkmanite, but differs distinctly from both.

Physical and Optical Properties: Color gray-black, streak black. $H=2$ to $2\frac{1}{2}$: $G=6.05$ (pycnometer). The mineral is very plastic. In the reflecting microscope, yenerite appears greenish next to galena. In oil it shows distinct pleochroism and strong anisotropy (in oil brownish bright gray to bluish dark gray, in air greenish-brown). No cleavage was observed.

Occurrence: A common mineral in the ore deposit of Işikdağ (N.N.W. of Ankara), occurring massive and as fine needles (max. length 5 mm., thickness .02–.05 mm.). Occurs alone and also intergrown with calcite, galena and quartz.

Discussion: It has not yet been demonstrated convincingly that falkmanite is distinct from boulangerite and this is likewise true of yenerite.

M. F.

Pseudoapatelite

André Magne: The apatelite of Meillet. *Bull. soc. franç. mineral.*, **65**, 39–42 (1942); through *Chem. Zentr.* (**1943**), II, 1083–1084. Magne describes a friable, bright yellow, earthy mineral from a quarry near La Souys. Analysis gave the formula $3Fe_2O_3\cdot4SO_3\cdot6H_2O$, corresponding to the apatelite of Meillet (1841) (but which contained much less H_2O. M.F.). The crystals appear rhombohedral and resemble jarosite. The mineral called apatelite by Lacroix (*Mineral. de la France*, **IV**, 246 (1910), which had the composition $(Fe,Al)_2O_3\cdot SO_3\cdot3H_2O$, is considered by Magne to be a different species and he proposes the name pseudoapatelite for it.

Discussion: These poorly defined minerals may be identical with borgströmite (1921) and with the artificial compound $3Fe_2O_3\cdot4SO_3\cdot9H_2O$, which is known to have the jarosite structure.

M. F.